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A NON-LINEAR LEAST-SQUARES APPROACH TO THE REFINEMENT OF ALL PARAMETERS INVOLVED IN ACID–BASE TITRATIONS

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Summary—A non-linear least-squares computer program has been written for the refinement of the parameters involved in potentiometric acid–base titrations. The program ACBA (ACid–BAse titrations) is applicable under quite general conditions to solutions containing one or more acids or bases. The method of refinement used gives the program several advantages over the other programs described previously.

Many papers have been published on the problem of determining the parameters involved in acid–base titrations (end-point, E^0, junction potential, analytical concentrations of reagents, protonation constants of weak acids, *etc.*).[1–35] The first approach used was the linearization of the titration curves, and many graphical methods have been proposed for the treatment of all types of acid–base titration.[1–16] In general the titration curves can be well interpreted by the use of computer programs which allow the calculation of the concentration of all the species in equilibrium,[17–21] as proposed by Anfalt *et al.*[19] Moreover, Anfalt *et al.*[22] have recently suggested that non-linear regression is a promising approach to end-point location, and some authors have already followed this suggestion.[23–30] The problem of analysing mixtures of weak acids or bases has also been overcome by both graphical and numerical methods.[31–35]

The first example of least-squares refinement of the parameters of an acid–base titration was given by Dyrssen *et al.*,[24] using the LETAGROP program.[36–39] This program, first set up for the refinement of formation constants, has been successively enlarged to deal with problems such as the refinement of the analytical concentrations.[39] However, since this program is large, and used for analysing more complicated systems, it does not seem to us efficient for analysing acid–base titrations.

To increase the possibilities of analysing potentiometric curves in acid–base titrations, we have written a non-linear least-squares computer program able to refine any parameter of such a titration, even in the case of mixtures. Moreover, parameters common to several titrations and parameters which have different values from titration to titration can be simultaneously refined with this program.

SYMBOLS

A_{ik}: analytical concentration of the ith ligand at the kth point of the titration
$C^0_{A_i}$: initial concentration of the ith ligand
$C^T_{A_i}$: concentration of the ith ligand in the titrant
a_{ik}: free concentration of ith ligand
H_k: analytical proton concentration
h_k: free proton concentration
C^0_H and C^T_H as for the ligand(s)
V_0: initial volume
v_k: titrant volume added
F: dilution factor
E_k: emf (mV)
K^H_{ij}: stepwise protonation constant
β^H_{ij}: overall protonation constant
K_w: ionic product of water
T: temperature (K)

EXPERIMENTAL

All the products used were of analytical-grade purity. The solutions were prepared with twice-distilled water.

Apparatus

The potentiometric titrations were done with an Orion 801-A pH-meter equipped with an EIL glass electrode and three different types of reference electrodes: (*a*) double-junction Ingold 303-90-NS, (*b*) single-junction Ingold 303-NS, (*c*) Orion 90-02-00. In the double-junction electrodes the outer sleve was filled with the ionic medium used in the titrations.

Further details of the potentiometric measurements made in this laboratory are reported elsewhere.[40–44]

THE PROGRAM

The relationships between the various parameters in acid–base titrations are

$$A = a\sum_{j=0}^{N}\beta_j h^j = (C_A^0 F_A V_0 + C_A^T v)/(v + V_0) \quad (1)$$

$$H = h + a\sum_{j=1}^{N} j\beta_j h^j = (C_H^0 F_H V_0 + C_H^T v)/(v + V_0) \quad (2)$$

$$E = E^0 + 0.19841\,T\log(h) + j_a h = E^0 + s_L \log(h) + j_a h. \quad (3)$$

Equations (1)–(3) can be combined to obtain an explicit equation for the titration volume

$$v = f(E; C^0, C^T, K_w, K_{ij}^H, E^0, s_L, j_a) = f(E; \mathbf{p}) \quad (4)$$

The parameters **p** are refined by the least-squares method,[45] minimizing the error-squares sum

$$U = \Sigma(v_{exp} - v_{calc})^2 = \Sigma s^2 \quad (5)$$

and at the optimum we have

$$\delta U/\delta p_n = 0 \quad (6)$$

where p_n is the nth parameter to be refined.

Defining the vectors $\mathbf{e} = \{p'_n - p_n\}$ (where p'_n is an estimate of the parameter p_n), $\mathbf{s} = \{s_k\}$ and the matrix $\mathbf{A} = \{\delta v_k/\delta p_n\}$, gives rise to the system of normal equations

$$(\mathbf{A}^T\mathbf{A})\mathbf{e} = \mathbf{As};\ \mathbf{Bx} = \mathbf{c} \quad (7)$$

$$(\mathbf{A}^T\mathbf{A})^{-1}\mathbf{As} = \mathbf{e};\ \mathbf{B}^{-1}\mathbf{C} = \mathbf{x} \quad (8)$$

The new parameters having been obtained, the calculations are repeated until the shifts are lower than a previously set tolerance.

It was decided to minimize the error-squares sum for the added titrant volume (instead of E or H) because (*i*) the derivatives $\delta v/\delta p_n$ can be obtained analytically and therefore the errors of numerical approximations are avoided, (*ii*) all the points have approximately equal weight.

To overcome the difficulties of ill-conditioning in the equations (7) due to scale, the matrix **B** and the vector **C** are scaled.[46] To overcome the difficulties of near singularities and indefiniteness of the scaled matrix $\mathbf{B}'^{-1}$ we analysed **B**′ into eigenvalues and their corresponding normalized eigen vectors and the element b'_{ij} of the inverse matrix can be obtained from the equation[47]

$$b'_{ij} = \sum_{k=1}^{m} \lambda_k^{-1} V_{ik} V_{jk} \quad (9)$$

(λ eigenvalues, V eigenvectors). The method used in this work to solve normal equations has been successfully adopted in solving other problems.[20,48,49]

* It is necessary to take into consideration the fact that not *all* the parameters in a titration can be refined simultaneously, otherwise completely false results can be obtained.[39]

The computer program ACBA, based on the method above, was written in FORTRAN IV and consists of the MAIN program and eight subroutines.

MAIN Controls the work of the whole program and in particular: (*i*) divides the parameters to be refined into common parameters (parameters common to all the titrations) and titration parameters (parameters relevant to a single titration); (*ii*) the shifts having been obtained, calculates new parameters; (*iii*) performs the convergence controls.

DATI Reads all the data relative to the titrations.

OUT Prints out the initial data and the results of the refinement.

HH Calculates by iteration, from (3), h and the derivatives $\delta h/\delta E^0$, $\delta h/\delta j_a$ and $\delta h/\delta s_L$.

DERIV Calculates the derivatives $\delta v/\delta p_n$.

SHIFT Constructs the matrix of the coefficients **B** and the vector **C**; calculates the shifts after recalling the subroutines SCALE, JACOBI and MIAVA.

SCALE Scales the matrix **B** and the vector **C**.[46]

JACOBI Calculates the eigenvalues and the eigenvectors by Jacobi's method.[50]

MIAVA Inverts the matrix **B**′ by using the equation (9).

RESULTS AND DISCUSSION

The program ACBA has been checked for a great many cases. Its first version (which could refine only a few parameters, and could not treat mixtures) has already been extensively used in previous work,[42–45,51] mostly to determine titrimetrically the purity of acids and to calculate E^0, j_a and s_L in order to calibrate and check the glass/calomel electrodes. In the present completed version all the possibilities of the program ACBA have been taken into consideration, that is, it has been used to refine different set of parameters* (up to nine common and two titration parameters) simultaneously in solutions containing one or more acids or bases.

Table 1. Results of two titrations of mixtures of acids or bases at 25°C and $I = 0.1M$ ($NaClO_4$)

		Taken	Found	Error
Mixture I*				
$HClO_4$ (mM)		0.495	0.580	+17.2%
malonic acid (mM)		1.452	1.422	− 2.1%
succinic acid (mM)		1.277	1.270	− 0.5%
phthalic acid (mM)		0.905	0.876	− 3.2%
total acid (mM)		7.763	7.716	− 0.6%
malonic acid	pK_1	2.623	2.66 ± 0.02	+ 0.04
	pK_2	5.250	5.26 ± 0.02	+ 0.01
succinic acid	pK_1	4.018	4.01 ± 0.01	− 0.01
	pK_2	5.147	5.08 ± 0.01	− 0.07
phthalic acid	pK_1	2.745	2.67 ± 0.01	− 0.08
	pK_2	4.920	5.06 ± 0.01	+ 0.14
Mixture II†				
pyridine (mM)		1.543	1.549	+ 0.4%
2,2′-bipyridyl (mM)		1.872	1.865	− 0.4%
total base (mM)		3.415	3.414	0.0%

* Two titrations; titrant 0.2500M NaOH.
† One titration; titrant 0.0997M $HClO_4$.

The refined results for two titrations of mixtures of acid or bases are reported in Table 1. In potentiometric acid–base titrations it has been noted that taking as known only one of the concentrations (that of the titrant or that of the titrand) gave a remarkable improvement in the fit, even when the difference between the refined and the estimated concentration was not at first very significant. In fact even small errors in the analytical concentrations can notably influence some parameters, for example the junction potential or the ionic product of water. Cross-titrations of acids and bases with a single primary standard have been shown, by the use of the program ACBA, to be very efficient for the standardization of all reagents with acid–base characteristics used in the experiments on solution equilibria carried out in our laboratory. Without modifications this program has also been used to test the response of a copper-selective electrode (the calculated slope, at 25°, was 29.7 ± 0.2 mV/pCu).

Generally (as may be seen in the examples reported in Table 1) the agreement between the known and calculated values is very good and, moreover, when E^0 is refined simultaneously with the other parameters, no calibration of the electrodes is necessary.*

In conclusion, it can be said that the amount of information that can be drawn from an acid–base potentiometric titration with an appropriate calculation method is far superior to that obtained by traditional graphical methods.

Some remarks must be made about the program: (*i*) the input and ordering of the data are structured in such a way that almost all kinds of acid–base potentiometric titrations can be analysed; (*ii*) the inversion of the matrix by the method described has allowed the convergence of the iterative process even in critical situations (many parameters to be refined, estimates of the parameters very approximate); (*iii*) the refinement is carried out on the parameter values and not on the logarithms of the values, as is often the case, to bring all parameters on to a scale of comparable magnitude (Gans and Vacca[52] have shown that the refinement is intrinsically ill-conditioned when the logarithms are refined); this can be done, not withstanding the enormous difference in the orders of magnitude of the various parameters, by scaling the matrix of the coefficients.

All calculations were carried out by means of a CDC CYBER 7600 computer. The appendix gives the data input instructions, the program, and two examples.

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APPENDIX

DATA INPUT INSTRUCTIONS FOR ACBA

(1) 1 card Format (20A4): TITLE; descriptive title (job)
(2) 1 card Format (312,12A5): NC,NL,NVAR, (PVAR (I), I = 1,NVAR);
NC: maximum number of iteration cycles to be performed
NL: number of ligands
NVAR: number of common parameters to be refined
PVAR (I): symbols of common parameters to be refined
COH: initial concn. of the strong acid (positive) or base (negative)
CTH: concn. of the strong acid (positive) or base (negative) in the titrant
EO: standard potential
KWL: log $K_w = -pK_w$
JA: j_a (coefficient of junction potential $E_j = j_a h$)
SL: s_t
COL 1, COL 2...: initial concentrations of ligands
CTL 1, CTL 2...: concentrations of the ligands in the titrant
K11, K12...K21...K31...: log K_{ij}^H (stepwise association constants)
(3) NL cards Format (5F10.0): ((KL(I,K), K = 1,5), I = 1,NL); (only if NL > 0)
KL(K,K): log K_{ij}^H
(4) 1 card Format (2F10.0): TEMP, KWL; temperature °C, $-pK_w$

The following cards for each titration curve
(5) 1 card Format (20A4): descriptive title (titration curve)
(6) 1 card Format (2F10.0, 3F7.0, F10.0, 2F7.0, I3): VX(1), VX(2), VO,
VX(3), VX(5), FDILH, VIN, DV, NA;
VX(1) = COH [see item (2)]
VX(2) = CTH
VO: initial volume
VX(3) = EO
VX(5) = JA
FDILH: dilution factor for COH (to allow overall refinement of the original concn. of a solution which has been titrated at different dilutions)
VIN = V_0; DV = v_a; NA = N [see item (9)]
(7) NL cards Format (2F10.0, 212, F10.0): VX(J), VX(J + 1), NNPO(L,K),
NNPT(L,K), FDILLM(L,K); only if NL > 0
VX(J) = COL (see item (2))
VX(J + 1) = CTL
NNPO: number of protons in the ligand (titrand)
NNPT: number of protons in the ligand (titrant)
FDILLM: dilution factor for COL [see item (6)]
(8) 1 card Format (I2, 12A5): NVART, (PVAR(K), K = 1, NVART);
NVART: number of titration parameters to be refined
PVAR(K): symbols of parameters to be refined [see item (2)]
(9) cards Format (5(2F7.0, I1): (VV(K), EE(K), INDEX(K), K = 1,5); (if DV = 0)
VV(K): titrant volume added (ml)
EE(K): e.m.f. (mV); if EO = 0 EE(K) = pH
INDEX(K): = 0 normal; = 1 indicates the end of a titration curve, GOTO (5)
(9) cards Format (−): (KE(K), K = 1, NA); without format, but expressed as an integer. (if DV > 0)
KE(K): e.m.f. = 10^{-1}KE or (if EO = 0) pH = 10^{-3}KE
The titrant volume added is: $v = V_0 + k \cdot va$ $k = 0$ ... NA [see item (6)] for a titration curve with constant increment of titrant.
When K = NA GOTO (5)
(10) 2 blank cards: end of all titration curves
4 blank cards: for the termination of the run
Concentrations: mole/l.
Volumes: ml
e.m.f.: mV

PROGRAM

```
      PROGRAM ACBA(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)                    1
C                                                                            2
C  THIS PROGRAM REFINES THE PARAMETERS OF ONE OR MORE ACID-BASE TITRATIONS    3
C                                                                            4
C  CARMELO RIGAMO - SEMINARIO MATEMATICO                                     5
C  GIUSEPPE ARENA, ENRICO RIZZARELLI, SILVIO SAMMARTANO - ISTITUTO DI        6
C  CHIMICA GENERALE          UNIVERSITATA DI CATANIA (1977)                  7
C                                                                            8
      DIMENSION KVAR(12),B(4,5),NB(4),NNPO(20,4),NNPT(20,4),FDILLM(20,4)     9
     &,FDILHM(20),IVT(20,6),X(20,14),VVO(20),NVT(20),SVQ(20),V(700),E(70     10
     &0),LAST(20),NP(20),IVAR(12),XM(12),BM(4,5),TOLL(12),COL(4),CTL(4),     11
     &FDILL(4),A1M(4),A2M(4),AM(4),DAH(4),PH(700),DV(700),Z(700,4),A2K(4     12
     &,5),A1K(4,5),SH(12),SIGX(12),XPT(34),SIGT(34),XPP(20,14),SIGP(20,1     13
     &4),DEVS(20),RL(20),NPO(4),NPT(4),D(700,12),DER(12)                     14
      REAL KP(4,5),LIM(12),NUM,JA,KW                                         15
C                                                                            16
C  CAN VARY COMMON PARAMETERS WITHOUT VARYING THE TITRATION PARAMETERS       17
C  THE JOB STARTS OFF BY VARYING THE COMMON PARAMETERS                       18
C                                                                            19
   70 CALL DATI(NC,NL,NVAR,SVQ,KVAR,KP,B,NB,X,VVO,FDILHM,FDILLM,NNPO,       20
     &NNPT,NVT,IVT,LEV2,V,E,LAST,NP,NTP,NTIT,AL10,JB,SVQT)                   21
C                                                                            22
C  LEV=1 REFINES THE PARAMETERS TO BE VARIED SIMULTANEOUSLY                  23
C  IN ALL TITRATIONS                                                         24
C  LEV=2 REFINES THE PARAMETERS TO BE VARIED IN EACH TITRATION               25
C                                                                            26
      ISDV=0                                                                 27
      NCGP=0                                                                 28
      LEV=1                                                                  29
      NCG=1                                                                  30
      NCICP=NC*2                                                             31
   82 NCC=0                                                                  32
   81 MLEV=0                                                                 33
   54 L=1                                                                    34
      K1=1                                                                   35
      IF(LEV.EQ.2) GOTO 35                                                   36
      IF(ISDV.EQ.1) GOTO 52                                                  37
      N=NTP                                                                  38
      NV=NVAR                                                                39
      SV2=SVQT                                                               40
      DO 36 K=1,NV                                                           41
   36 IVAR(K)=KVAR(K)                                                        42
      GOTO 51                                                                43
   35 IF(NVT(L).EQ.0) GOTO 83                                                44
      NCC=0                                                                  45
      N=NP(L)                                                                46
      NV=NVT(L)                                                              47
      SV2=SVQ(L)                                                             48
      DO 37 K=1,NV                                                           49
   37 IVAR(K)=IVT(L,K)                                                       50
   51 JAV=0                                                                  51
      JEQ=0                                                                  52
      JVH=0                                                                  53
      JSL=0                                                                  54
C  MEMORIZES THE ESTIMATES OF PARAMETERS TO BE REFINED                       55
      DO 4 I=1,NV                                                            56
      K=IVAR(I)                                                              57
      IF(NCC.GT.0) GOTO 10                                                   58
      IF(K.LT.15) GOTO 92                                                    59
      L1=(K-10)/5                                                            60
      L2=K-9-L1*5                                                            61
      XM(I)=KP(L1,L2)                                                        62
      BM(L1,L2)=B(L1,L2)                                                     63
      GOTO 4                                                                 64
   92 XM(I)=X(L,K)                                                           65
   10 IF(K.NE.3) GOTO 20                                                     66
      JEQ=1                                                                  67
      GOTO 25                                                                68
   20 IF(K.NE.5) GOTO 71                                                     69
      JAV=1                                                                  70
      GOTO 25                                                                71
   71 IF(K.NE.6) GOTO 4                                                      72
      JSL=1                                                                  73
   25 JVH=1                                                                  74
    4 CONTINUE                                                               75
C  FIXES LIMITS AND TOLERANCES OF THE SHIFTS                                 76
   86 DO 73 I=1,NV                                                           77
      K=IVAR(I)                                                              78
      IF(K.LT.15) GOTO 79                                                    79
      L1=(K-10)/5                                                            80
      L2=K-9-L1*5                                                            81
      XL=KP(L1,L2)                                                           82
      GOTO 9                                                                 83
   79 XL=ABS(X(L,K))                                                         84
      IF(K.EQ.3) GOTO 14                                                     85
      IF(XL.GT.0.) GOTO 1                                                    86
      LIM(I)=1.E-6                                                           87
      GOTO 73                                                                88
   14 LIM(I)=5.                                                              89
      GOTO 73                                                                90
```

```
      1 IF(K.NE.5) GOTO 9                                                    91
        LIM(I)=0.5*XL                                                        92
        GOTO 73                                                              93
      9 LIM(I)=0.1*XL                                                        94
     73 TOLL(I)=0.0001*XL                                                    95
        NCC=NCC+1                                                            96
     52 COH=X(L,1)                                                           97
        CTH=X(L,2)                                                           98
        EO=X(L,3)                                                            99
        KW=X(L,4)                                                           100
        JA=X(L,5)                                                           101
        SL=X(L,6)/AL10                                                      102
        VO=VVO(L)                                                           103
        FDILH=FDILHM(L)                                                     104
        K2=LAST(L)                                                          105
        DO 26 K=K1,K2                                                       106
        IF(EO.GT.0)GO TO 16                                                 107
        PHO=-E(K)*AL10                                                      108
        GO TO 21                                                            109
     16 PHO=(E(K)-EO)/SL                                                    110
     21 H=EXP(PHO)                                                          111
        DHEO=-H/SL                                                          112
        DHJA=0.                                                             113
        DHSL=-H*PHO/SL                                                      114
        IF(JA.EQ.0.) GOTO 89                                                115
C    CALCULATES H VALUE AND THE DERIVATIVES OF H WITH RESPECT TO EO, JA, SL 116
        CALL HH(JA,PHO,SL,H,JAV,JEO,JSL,DHEO,DHJA,DHSL)                     117
     89 HQ=H*H                                                              118
        SAN1CO=0.                                                           119
        SAN2CT=0.                                                           120
        SDAHCO=0.                                                           121
        SDAHCT=0.                                                           122
        IF(NL.EQ.0) GOTO 24                                                 123
        DO 29 J=1,NL                                                        124
        I=J*2+5                                                             125
        COL(J)=X(L,I)                                                       126
        CTL(J)=X(L,I+1)                                                     127
        NPO(J)=NNPO(L,J)                                                    128
        NPT(J)=NNPT(L,J)                                                    129
        FDILL(J)=FDILLM(L,J)                                                130
        A1=0.                                                               131
        DA1=0.                                                              132
        DA2=0.                                                              133
        A2=1.                                                               134
        NBL=NB(J)                                                           135
        DO 30 I=1,NBL                                                       136
        BH=B(J,I)*H**I                                                      137
        DA1=DA1+I*I*BH/H                                                    138
        DA2=DA2+I*BH/H                                                      139
        A1=A1+I*BH                                                          140
     30 A2=A2+BH                                                            141
        A2Q=A2*A2                                                           142
        A1M(J)=A1                                                           143
        A2M(J)=A2                                                           144
        AM(J)=A1/A2                                                         145
        DAH(J)=(DA1*A2-DA2*A1)/A2Q                                          146
        SAN1CO=SAN1CO+(AM(J)-NPO(J))*COL(J)*FDILL(J)                        147
        SAN2CT=SAN2CT+(AM(J)-NPT(J))*CTL(J)                                 148
        SDAHCO=SDAHCO+DAH(J)*COL(J)*FDILL(J)                                149
     29 SDAHCT=SDAHCT+DAH(J)*CTL(J)                                         150
     24 NUM=VO*(SAN1CO+H-KW/H-COH*FDILH)                                    151
        DEN=KW/H-H-SAN2CT+CTH                                               152
        DENQ=DEN*DEN                                                        153
        VC=NUM/DEN                                                          154
        DV(K)=VC-V(K)                                                       155
        IF(JVH.EQ.0) GOTO 6                                                 156
        DVH=(VO*(SDAHCO+1.+KW/HQ)*DEN+(KW/HQ+1.+SDAHCT)*NUM)/DENQ           157
      6 IF(ISDV.EQ.1) GOTO 26                                               158
        IF(NCG.LE.NC.AND.NCG.GT.0) GOTO 60                                  159
        IF(EO.GT.0.)GO TO 97                                                160
        PH(K)=E(K)                                                          161
        GO TO 98                                                            162
     97 PH(K)=-ALOG(H)/AL10                                                 163
     98 IF(NL.EQ.0)GO TO 26                                                 164
        DO 18 J=1,NL                                                        165
     18 Z(K,J)=AM(J)                                                        166
        GOTO 26                                                             167
     60 IF(JB*LEV.NE.1) GOTO 7                                              168
        DO 17 IK=1,NL                                                       169
        NBL=NB(IK)                                                          170
        A2K(IK,NBL)=B(IK,NBL)*H**NBL                                        171
        A1K(IK,NBL)=NBL*A2K(IK,NBL)                                         172
        IF(NBL.EQ.1) GOTO 17                                                173
        DO 58 I=2,NBL                                                       174
        J=NBL+1-I                                                           175
        BH=B(IK,J)*H**J                                                     176
        A1K(IK,J)=A1K(IK,J+1)+J*BH                                          177
     58 A2K(IK,J)=A2K(IK,J+1)+BH                                            178
     17 CONTINUE                                                            179
C    CALCULATES THE DERIVATIVES OF V WITH RESPECT TO THE PARAMETERS         180
C    TO BE REFINED                                                          181
      7 CALL DERIV(NV,IVAR,VO,FDILH,DEN,NUM,DENQ,DHEO,H,DVH,DHJA,DHSL,      182
     &AM,NPO,FDILL,NPT,COL,CTL,A1K,A2M,A2K,A1M,KP,DER)                      183
        DO 33 I=1,NV                                                        184
```

```
   33 D(K,I)=DER(I)                                                    185
   26 CONTINUE                                                         186
      IF(LEV.EQ.2) GOTO 39                                             187
      IF(L.EQ.NTIT) GOTO 15                                            188
      L=L+1                                                            189
      K1=K2+1                                                          190
      GOTO 52                                                          191
C  CALCULATES STANDARD DEVIATIONS AND R(HAMILTON)                      192
   15 K1=1                                                             193
   39 SDV2=0.                                                          194
      DO 41 K=K1,K2                                                    195
   41 SDV2=SDV2+DV(K)*DV(K)                                            196
      R=SQRT(SDV2/SV2)                                                 197
      SDV=SQRT(SDV2/(N-NV))                                            198
      IF(ISDV.EQ.1) GOTO 56                                            199
      IF(NCG.EQ.0) GOTO 80                                             200
      IF(NCG+LEV+NCC.EQ.1) WRITE(6,105) SDV,R                          201
  105 FORMAT(/* ST.DEV.=*E10.3,5X*R(HAMILTON)=*E10.3,5X*WITH THE INPUT D  202
     &ATA*/)                                                           203
C  CALCULATES THE SHIFTS                                               204
      CALL SHIFT(NV,K1,K2,DV,D,SH,SIGX)                                205
C  COMPARES THE SHIFTS WITH LIMITS AND TOLERANCES                      206
      M=0                                                              207
      DO 40 I=1,NV                                                     208
      IF(ABS(SH(I)).LE.TOLL(I)) GOTO 40                                209
      M=1                                                              210
      MLEV=1                                                           211
      IF(SH(I).LT.(-LIM(I))) SH(I)=-LIM(I)                             212
      IF(SH(I).GT.LIM(I)) SH(I)=LIM(I)                                 213
   40 CONTINUE                                                         214
      IF(M.EQ.1.AND.NCC.LT.NCICP) GOTO 91                              215
      NCIC=NCC                                                         216
      NCC=NCICP                                                        217
      IF(NCIC.LT.NCICP) GOTO 91                                        218
C  IF THE CYCLE DOES NOT CONVERGE, ASSIGNS TO THE PARAMETERS THE VALUE OF  219
C  THE PREVIOUS CYCLE                                                  220
      IF(LEV.EQ.2) GOTO 67                                             221
      DO 66 K=1,NV                                                     222
      J=IVAR(K)                                                        223
      IF(J.LT.15) GOTO 11                                              224
      L1=(J-10)/5                                                      225
      L2=J-9-L1*5                                                      226
      KP(L1,L2)=XM(K)                                                  227
      B(L1,L2)=BM(L1,L2)                                               228
      GOTO 66                                                          229
   11 DO 96 L=1,NTIT                                                   230
   96 X(L,J)=XM(K)                                                     231
   66 SIGT(J)=0.                                                       232
      GOTO 8                                                           233
   67 DO 68 K=1,NV                                                     234
      J=IVAR(K)                                                        235
      SIGP(L,J)=0.                                                     236
      DEVS(L)=0.                                                       237
      RL(L)=0.                                                         238
   68 X(L,J)=XM(K)                                                     239
      GOTO 83                                                          240
   91 IF(NCG.EQ.1.OR.LEV.EQ.2) GOTO 3                                  241
      IF(SDV2.LE.SDV2M) GOTO 3                                         242
      DO 2 I=1,NV                                                      243
    2 SH(I)=SH(I)/3.                                                   244
   GIVES THE PARAMETERS AN INCREMENT EQUAL TO THE CALCULATED SHIFT     245
    3 DO 85 I=1,NV                                                     246
      K=IVAR(I)                                                        247
      XX=SH(I)                                                         248
      IF(K.LT.15) GOTO 19                                              249
      L1=(K-10)/5                                                      250
      L2=K-9-L1*5                                                      251
      KP(L1,L2)=KP(L1,L2)+XX                                           252
      XV=KP(L1,L2)                                                     253
   65 SIGX(I)=SIGX(I)/(AL10*XV)                                        254
      XV=ALOG(XV)/AL10                                                 255
      GOTO 50                                                          256
   19 X(L,K)=X(L,K)+XX                                                 257
      XV=X(L,K)                                                        258
      IF(LEV.EQ.2) GOTO 88                                             259
      DO 77 J=1,NTIT                                                   260
   77 X(J,K)=XV                                                        261
   88 IF(K.EQ.4) GOTO 65                                               262
   50 IF(LEV.EQ.1) GOTO 62                                             263
      XPP(L,K)=XV                                                      264
      SIGP(L,K)=SIGX(I)                                                265
      GOTO 85                                                          266
   62 XPT(K)=XV                                                        267
      SIGT(K)=SIGX(I)                                                  268
   85 CONTINUE                                                         269
      IF(LEV.EQ.2) GOTO 59                                             270
      IF(JB.EQ.0) GOTO 38                                              271
      DO 57 K=1,NL                                                     272
      NBL=NB(K)                                                        273
      BL=1.                                                            274
      DO 57 I=1,NBL                                                    275
```

```
      BL=BL+KP(K,I)                                                    276
   57 B(K,I)=BL                                                        277
      GOTO 38                                                          278
   59 IF(M.EQ.1) GOTO 86                                               279
      ISDV=1                                                           280
      GOTO 52                                                          281
   83 IF(L.EQ.NTIT) GOTO 84                                            282
      L=L+1                                                            283
      K1=K2+1                                                          284
      K2=LAST(L)                                                       285
      GOTO 35                                                          286
   38 IF(M.EQ.1) GOTO 81                                               287
    8 IF(NCIC.EQ.1.AND.NCG.GT.1) GOTO 28                               288
      ISDV=1                                                           289
      GOTO 54                                                          290
   84 LEV=1                                                            291
      IF(MLEV.EQ.0.OR.NCG.EQ.NC) GOTO 28                               292
      NCG=NCG+1                                                        293
      GOTO 82                                                          294
   22 NCGP=NCIC                                                        295
      NC=NCICP                                                         296
      GO TO 23                                                         297
   28 NCGP=NCG                                                         298
   23 NCG=0                                                            299
      GOTO 81                                                          300
   56 ISDV=0                                                           301
      IF(LEV2.EQ.0) GOTO 22                                            302
      IF(LEV.EQ.1) GOTO 12                                             303
      DO 78 I=1,NV                                                     304
      K=IVAR(I)                                                        305
   78 SIGP(L,K)=SIGP(L,K)+SDV                                          306
      DEVS(L)=SDV                                                      307
      RL(L)=R                                                          308
      GOTO 83                                                          309
   12 IF(NCG.EQ.1) GOTO 99                                             310
      IF(ABS(SDV2-SDV2M)/SDV2.LE.0.0001) GOTO 28                       311
   99 SDV2M=SDV2                                                       312
      IF(LEV2.EQ.0) GOTO 28                                            313
      LEV=2                                                            314
      GOTO 81                                                          315
   80 CALL OUT(NTIT,NVT,DEVS,RL,IVT,SIGP,XPP,NCGP,NC,SDV,R,NVAR,KVAR,  316
     &SIGT,XPT,NL,LAST,NTP,V,DV,E,PH,Z)                                317
      GOTO 70                                                          318
      END                                                              319
      SUBROUTINE OUT(NTIT,NVT,DEVS,RL,IVT,SIGP,XPP,NCGP,NC,SDV,R,NVAR, 320
     &KVAR,SIGT,XPT,NL,LAST,NTP,V,DV,E,PH,Z)                           321
C                                                                      322
C  THIS ROUTINE PRINTS OUT THE RESULTS                                 323
C                                                                      324
      DIMENSION NVT(20),DEVS(20),RL(20),IVT(20,6),SIGP(20,14),XPP(20,14),325
     &VAR(34),KVAR(12),SIGT(34),XPT(34),V(700),DV(700),E(700),PH(700), 326
     &Z(700,4),LAST(12)                                                327
      DATA VAR/3HCOH,3HCTH,2HEO,3HKWL,2HJA,2HSL,4HCOL1,4HCTL1,4HCOL2,4HC328
     &TL2,4HCOL3,4HCTL3,4HCOL4,4HCTL4,3HK11,3HK12,3HK13,3HK14,3HK15,3HK2329
     &1,3HK22,3HK23,3HK24,3HK25,3HK31,3HK32,3HK33,3HK34,3HK35,3HK41,3HK4330
     &2,3HK43,3HK44,3HK45/                                             331
      DATA VARZ/1HZ/                                                   332
      DO 64 L=1,NTIT                                                   333
      N=NVT(L)                                                         334
      IF(N.EQ.0) GOTO 64                                               335
      WRITE(6,113) L,DEVS(L),RL(L)                                     336
  113 FORMAT(//* TITRATION*I3,5X*ST.DEV.=*E10.3,5X*R(HAMILTON)=*E10.3) 337
      WRITE(6,116)                                                     338
  116 FORMAT(/28X*VALUE*13X*ST.DEV.*/)                                 339
      DO 23 I=1,N                                                      340
      K=IVT(L,I)                                                       341
   23 WRITE(6,115) VAR(K),XPP(L,K),SIGP(L,K)                           342
  115 FORMAT(17X,A4,F15.7,5X,E14.7)                                    343
   64 CONTINUE                                                         344
      IF(NCGP.GE.NC) WRITE(6,117)                                      345
  117 FORMAT(/* MAXIMUM NO. OF ITERATIONS PERFORMED*)                  346
      WRITE(6,107) NCGP,SDV,R                                          347
  107 FORMAT(/* CYCLE N.*I3,7X*ST.DEV.=*E10.3,5X*R(HAMILTON)=*E10.3)   348
      WRITE(6,116)                                                     349
      DO 16 I=1,NVAR                                                   350
      K=KVAR(I)                                                        351
      SIGT(K)=SIGT(K)*SDV                                              352
   16 WRITE(6,115) VAR(K),XPT(K),SIGT(K)                               353
      WRITE(6,121)                                                     354
  121 FORMAT(/11X*V*6X*DV*6X*E*6X*PH*)                                 355
      IF(NL.GT.0) WRITE(6,123) (VARZ,K,K=1,NL)                         356
  123 FORMAT(1H+35X4(4XA1,I1))                                         357
      WRITE(6,124)                                                     358
  124 FORMAT(1H+/)                                                     359
      L=1                                                              360
      L1=1                                                             361
      DO 14 K=1,NTP                                                    362
      WRITE(6,122) V(K),DV(K),PH(K)                                    363
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```
  122 FORMAT(5X,F9.4,F7.4,8X,F7.3)                                        364
      IF(E(K).NE.PH(K))WRITE(6,125)E(K)                                   365
  125 FORMAT(1H+20XF8.2)                                                  366
      IF(K.LT.L1) GOTO 10                                                 367
      WRITE(6,120) L                                                      368
  120 FORMAT(1H+,I4)                                                      369
      L1=LAST(L)+1                                                        370
      L=L+1                                                               371
   10 IF(NL.GT.0) WRITE(6,118) (Z(K,J),J=1,NL)                            372
  118 FORMAT(1H+,36X4F6.3)                                                373
   14 CONTINUE                                                            374
      RETURN                                                              375
      END                                                                 376
      SUBROUTINE SHIFT(NV,K1,K2,DV,D,SH,SIGX)                             377
C                                                                         378
C  THIS ROUTINE CALCULATES THE MATRIX OF THE COEFFICIENTS IN ORDER TO      379
C  DETERMINE THE SHIFTS                                                   380
C                                                                         381
      DIMENSION CK(12),C(12,12),DV(700),D(700,12),SH(12),SIGX(12)         382
     &,QAST(12,12),BAST(12),VAL(12),VEC(12,12),XAST(12),DIAG(12)          383
      DO 22 I=1,NV                                                        384
      CK(I)=0.                                                            385
      DO 22 J=1,NV                                                        386
   22 C(I,J)=0.                                                           387
      DO 31 K=K1,K2                                                       388
      DO 31 I=1,NV                                                        389
      CK(I)=CK(I)-DV(K)*D(K,I)                                            390
      DO 31 J=1,NV                                                        391
   31 C(I,J)=C(I,J)+D(K,I)*D(K,J)                                         392
      IF(NV.GT.1) GOTO 32                                                 393
      SH(1)=CK(1)/C(1,1)                                                  394
      SIGX(1)=1./SQRT(C(1,1))                                             395
      RETURN                                                              396
C  RECALLS THE SUBROUTINES CONCERNING THE SHIFT CALCULATION               397
   32 CALL SCALE(NV,C,CK,QAST,BAST)                                       398
      CALL JACOBI(NV,QAST,VAL,VEC)                                        399
      CALL MIAVA(NV,VAL,VEC,BAST,XAST,DIAG)                               400
C  CALCULATES SHIFTS AND RELATIVE STANDARD DEVIATIONS                     401
      DO 15 I=1,NV                                                        402
      SH(I)=XAST(I)/SQRT(C(I,I))                                          403
   15 SIGX(I)=SQRT(DIAG(I)/C(I,I))                                        404
      RETURN                                                              405
      END                                                                 406
      SUBROUTINE DATI(NC,NL,NVAR,SVQ,KVAR,KP,B,NB,X,VVO,FDILHM,FDILLM,    407
     &NNPO,NNPT,NVT,IVT,LEV2,V,E,LAST,NP,NTP,NTIT,AL10,JB,SVQT)           408
C                                                                         409
C  THIS ROUTINE READS INPUT DATA                                          410
C                                                                         411
      DIMENSION TITLE(20),PVAR(12),VAR(34),KVAR(12),B(4,5),NB(4),VX(14),  412
     &NNPO(20,4),NNPT(20,4),FDILLM(20,4),X(20,14),VVO(20),FDILHM(20),     413
     &NVT(20),IVT(20,6),VV(5),EE(5),INDEX(5),V(700),E(700),LAST(20),      414
     &NP(20),SVQ(20),KE(700)                                              415
      REAL KL(4,5),KP(4,5),KWL                                            416
      DATA VAR/3HCOH,3HCTH,2HEO,3HKWL,2HJA,2HSL,4HCOL1,4HCTL1,4HCOL2,4HC   417
     &TL2,                                                                418
     &4HCOL3,4HCTL3,4HCOL4,4HCTL4,3HK11,3HK12,3HK13,3HK14,3HK15,3HK21,    419
     &3HK22,3HK23,3HK24,3HK25,3HK31,3HK32,3HK33,3HK34,3HK35,3HK41,3HK42,  420
     &3HK43,3HK44,3HK45/                                                  421
      AL10=ALOG(10.)                                                      422
      READ(5,100) TITLE                                                   423
  100 FORMAT(20A4)                                                        424
      READ(5,101) NC,NL,NVAR,(PVAR(I),I=1,NVAR)                           425
  101 FORMAT(3I2,12A5)                                                    426
C                                                                         427
C  NC=NO. OF CYCLES  -  NL=NO. OF LIGANDS                                 428
C  NVAR=NO. OF COMMON PARAMETERS TO BE REFINED                            429
C  PVAR=SYMBOLS OF COMMON PARAMETERS TO BE REFINED                        430
C  (COH,CTH,EO,KWL,JA,SL,COL1,CTL1,COL2,CTL2,COL3,CTL3,COL4,CTL4,K11,K12, 431
C   K13,K14,K15,K21,K22,K23,K24,K25,K31,K32,K33,K34,K35,K41,K42,K43,K44,K45) 432
C                                                                         433
      IF(NVAR.EQ.0) STOP                                                  434
      WRITE(6,102) TITLE                                                  435
  102 FORMAT(1H1,10X20A4/)                                                436
      JB=0                                                                437
      L1=1                                                                438
      DO 69 I=1,NVAR                                                      439
      DO 94 K=1,34                                                        440
      IF(PVAR(I).EQ.VAR(K)) GOTO 20                                       441
   94 CONTINUE                                                            442
   20 IF(K.GT.14) JB=1                                                    443
   69 KVAR(I)=K                                                           444
      IF(NL.EQ.0) GOTO 1                                                  445
      READ(5,103) ((KL(I,K),K=1,5),I=1,NL)                                446
  103 FORMAT(5F10.0)                                                      447
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C  KL= LOG(K)                                                          448
      DO 2 I=1,NL                                                      449
      BL=0.                                                            450
      DO 3 K=1,5                                                       451
      AKL=KL(I,K)                                                      452
      IF(AKL.EQ.0.) GOTO 2                                             453
      BL=BL+AKL                                                        454
      KP(I,K)=EXP(AL10*AKL)                                            455
      WRITE(6,104) I,K,AKL                                             456
  104 FORMAT(* LOG.K*2I1,**=*,F8.3)                                    457
    3 B(I,K)=EXP(AL10*BL)                                              458
    2 NB(I)=K-1                                                        459
    1 READ(5,103) TEMP,KWL                                             460
      VX(4)=EXP(AL10*KWL)                                              461
      VX(6)=0.086173*(273.15+TEMP)*AL10                                462
C  TEMP=TEMPERATURE  -  KWL=LOG(KW)  -  VX(4)=KW  -  VX(6)=SL          463
      WRITE(6,110) TEMP,VX(6),KWL                                      464
  110 FORMAT(/5X*TEMPERATURE=*F9.3/5X*SL=*F9.3/5X*KWL=*F8.3/)          465
      I=0                                                              466
      L=0                                                              467
      LEV2=0                                                           468
      SVQT=0.                                                          469
   75 READ(5,100) TITLE                                                470
      READ(5,112) VX(1),VX(2),VO,VX(3),VX(5),FDILH,VIN,DV,NA           471
  112 FORMAT(2F10.0,3F7.0,F10.0,2F7.0,I3)                              472
C                                                                      473
C  VX(1)=COH  -  VX(2)=CTH  -  VO=VOLUME  -  VX(3)=EO  -  VX(5)=JA     474
C  FDILH = DILUTION FACTOR FOR COH                                     475
C  VIN = VOLUME OF THE FIRST POINT OF THE TITRATION                    476
C  DV = INCREMENT OF THE VOLUME FOR THE FOLLOWING POINTS               477
C  NA = NUMBER OF POINTS IN THE TITRATION                              478
C                                                                      479
      IF(VO.EQ.0.) GOTO 76                                             480
      SV2=0.                                                           481
      L=L+1                                                            482
      WRITE(6,119) L,TITLE                                             483
  119 FORMAT(/* TITRATION*I3,5X20A4/)                                  484
      IF(FDILH.EQ.0..AND.VX(1).NE.0.) FDILH=1.                         485
      WRITE(6,109) VX(1),FDILH,VX(2),VO,VX(3),VX(5)                    486
  109 FORMAT(6X*COH =*F11.8,4X*FDILH=*F11.8,3X*CTH =*F11.8,3X*VO=*F8.3,487
     &3X*EO=*F8.3,3X*JA=*F8.3)                                         488
      IF(NL.EQ.0) GOTO 61                                              489
      DO 98 K=1,NL                                                     490
      J=2*K+5                                                          491
      READ(5,210) VX(J),VX(J+1),NNPO(L,K),NNPT(L,K),FDILLM(L,K)        492
  210 FORMAT(2F10.0,2I2,F10.0)                                         493
C                                                                      494
C  VX(J)=COL  -  VX(J+1)=CTL                                           495
C  NNPO = NUMBER OF PROTONS IN THE LIGAND (TITRATE)                    496
C  NNPT = NUMBER OF PROTONS IN THE LIGAND (TITRANT)                    497
C  FDILLM = DILUTION FACTOR FOR COL                                    498
C                                                                      499
      IF(FDILLM(L,K).EQ.0..AND.VX(J).NE.0.) FDILLM(L,K)=1.             500
   98 WRITE(6,108)K,VX(J),K,FDILLM(L,K),K,VX(J+1),K,NNPO(L,K),K,NNPT(L,K) 501
  108 FORMAT(6X*COL*I1,**=*F11.8,4X*FDIL*I1,**=*F11.8,3X*CTL*I1,**=*F11.8,502
     &3X,*NPO*I1,**=*I2,3X*NPT*I1,**=*I2)                              503
   61 READ(5,123) NVART,(PVAR(K),K=1,NVART)                            504
  123 FORMAT(I2,12A5)                                                  505
C  NVART=NO. OF PARAMETERS TO BE REFINED                               506
C  PVAR=SYMBOLS OF PARAMETERS TO BE REFINED                            507
      DO 74 J=1,14                                                     508
   74 X(L,J)=VX(J)                                                     509
      VVO(L)=VO                                                        510
      FDILHM(L)=FDILH                                                  511
      NVT(L)=NVART                                                     512
      IF(NVART.EQ.0) GOTO 4                                            513
      LEV2=1                                                           514
      DO 95 K=1,NVART                                                  515
      DO 97 J=1,14                                                     516
      IF(PVAR(K).EQ.VAR(J)) GOTO 95                                    517
   97 CONTINUE                                                         518
   95 IVT(L,K)=J                                                       519
    4 IF(DV.EQ.0.)GO TO 25                                             520
      READ(5,*)(KE(K),K=1,NA)                                          521
C                                                                      522
C  KE = EMF*10 (IF EO.GT.0) OR PH*1000 (IF EO=0)                       523
C  IF (KE=0 AND EO=0) OR (KE=9999 AND EO.GT.0) THE PAIR OF VALUES V,KE 524
C  IS NEGLECTED                                                        525
C                                                                      526
      DO 5 K=1,NA                                                      527
      IF(VX(3).GT.0.) GO TO 8                                          528
      IF(KE(K).EQ.0) GO TO 6                                           529
      I=I+1                                                            530
      E(I)=KE(K)*0.001                                                 531
      GO TO 7                                                          532
    8 IF(KE(K).EQ.9999) GO TO 6                                        533
      I=I+1                                                            534
      E(I)=KE(K)*0.1                                                   535
    7 V(I)=VIN                                                         536
      SV2=SV2+VIN*VIN                                                  537
    6 VIN=VIN+DV                                                       538
    5 CONTINUE                                                         539
      GO TO 72                                                         540
   25 READ(5,114) (VV(K),EE(K),INDEX(K),K=1,5)                         541
  114 FORMAT(5(2F7.2,I1))                                              542
```

```
C                                                                       543
C  VV = VOLUME   -   EE = EMF  (IF EO.GT.0)  OR  PH  (IF EO = 0)       544
C  INDEX = 0 NORMAL   -   INDEX = 1 END OF TITRATION                   545
C                                                                       546
      DO 71 K=1,5                                                       547
      IF(VV(K).EQ.0..AND.EE(K).EQ.0.) GOTO 71                           548
      I=I+1                                                             549
      V(I)=VV(K)                                                        550
      E(I)=EE(K)                                                        551
      SV2=SV2+V(I)*V(I)                                                 552
      IF(INDEX(K).EQ.1) GOTO 72                                         553
   71 CONTINUE                                                          554
      GOTO 25                                                           555
   72 N=I-L1+1                                                          556
      WRITE(6,111) N                                                    557
  111 FORMAT(/6X*NO. OF POINTS*I4/)                                     558
      L1=I+1                                                            559
      LAST(L)=I                                                         560
      NP(L)=N                                                           561
      SVQ(L)=SV2                                                        562
      SVQT=SVQT+SV2                                                     563
      GOTO 75                                                           564
   76 NTP=I                                                             565
      WRITE(6,120) NTP                                                  566
  120 FORMAT(/* TOTAL NO. OF POINTS*I4/)                                567
      NTIT=L                                                            568
      RETURN                                                            569
      END                                                               570
      SUBROUTINE HH(JA,PHO,SL,H,JAV,JEO,JSL,DHEO,DHJA,DHSL)             571
C                                                                       572
C  THIS ROUTINE CALCULATES THE DERIVATIVES OF H WITH RESPECT TO EO, JA, SL.  573
C  CALCULATES ALSO H-VALUE.                                             574
C                                                                       575
      REAL JA                                                           576
      PSI=PHO                                                           577
   63 PH1=PSI-JA*H/SL                                                   578
      H=EXP(PH1)                                                        579
      IF(JAV.EQ.0) GOTO 5                                               580
      DHJA=-H*(H+JA*DHJA)/SL                                            581
    5 IF(JEO.EQ.0) GOTO 75                                              582
      DHEO=-H*(1.+JA*DHEO)/SL                                           583
   75 IF(JSL.EQ.0) GOTO 3                                               584
      DHSL=H*(PSI*SL+JA*H)/(SL*SL)                                      585
    3 IF(ABS(PHO-PH1)/PH1.LT.0.0001) RETURN                             586
      PHO=PH1                                                           587
      GOTO 63                                                           588
      END                                                               589
      SUBROUTINE DERIV(NV,IVAR,VO,FDILH,DEN,NUM,DENQ,DHEO,H,DVH,        590
     &DHJA,DHSL,AM,NPO,FDILL,NPT,COL,CTL,A1K,A2M,A2K,A1M,KP,DER)        591
C                                                                       592
C  THIS ROUTINE CALCULATES THE DERIVATIVES OF V WITH RESPECT TO THE     593
C  PARAMETERS TO BE REFINED                                             594
C                                                                       595
      DIMENSION IVAR(12),AM(4),NPO(4),FDILL(4),NPT(4),COL(4),CTL(4)     596
     &,A1K(4,5),A2M(4),A2K(4,5),A1M(4),DER(12)                          597
      REAL KP(4,5),NUM                                                  598
      DO 33 I=1,NV                                                      599
      J=IVAR(I)                                                         600
      IF(J.GT.14) GOTO 49                                               601
      GOTO(41,42,43,44,45,46,47,48,47,48,47,48,47,48) J                 602
   41 DERV=-VO*FDILH/DEN                                                603
      GOTO 33                                                           604
   42 DERV=-NUM/DENQ                                                    605
      GOTO 33                                                           606
   43 DERV=DVH*DHEO                                                     607
      GOTO 33                                                           608
   44 DERV=-(VO*DEN+NUM)/(H*DENQ)                                       609
      GOTO 33                                                           610
   45 DERV=DVH*DHJA                                                     611
      GOTO 33                                                           612
   46 DERV=DVH*DHSL                                                     613
      GOTO 33                                                           614
   47 L1=(J-5)/2                                                        615
      DERV=VO*(AM(L1)-NPO(L1))*FDILL(L1)/DEN                            616
      GOTO 33                                                           617
   48 L1=(J-6)/2                                                        618
      DERV=NUM*(AM(L1)-NPT(L1))/DENQ                                    619
      GOTO 33                                                           620
   49 L1=(J-10)/5                                                       621
      L2=J-9-L1*5                                                       622
      DVA=(VO*COL(L1)*FDILL(L1)*DEN+CTL(L1)*NUM)/DENQ                   623
      DERV=DVA*(A1K(L1,L2)*A2M(L1)-A2K(L1,L2)*A1M(L1))/(KP(L1,L2)*A2M(L1  624
     &)**2)                                                             625
   33 DER(I)=DERV                                                       626
      RETURN                                                            627
      END                                                               628
```

```
      SUBROUTINE SCALE(N,Q,B,QAST,BAST)                                  629
C                                                                        630
C  THIS ROUTINE SCALES THE MATRIX Q AND THE VECTOR B                     631
C                                                                        632
      DIMENSION Q(12,12),QAST(12,12),BAST(12),B(12)                      633
      DO 2 I=1,N                                                         634
      QI=ABS(Q(I,I))                                                     635
      BAST(I)=B(I)/SQRT(QI)                                              636
      QAST(I,I)=1.                                                       637
      DO 3 K=1,N                                                         638
      IF(I.EQ.K) GOTO 3                                                  639
      QAST(I,K)=Q(I,K)/SQRT(QI*ABS(Q(K,K)))                              640
    3 CONTINUE                                                           641
    2 CONTINUE                                                           642
      RETURN                                                             643
      END                                                                644
      SUBROUTINE JACOBI(N,A,VAL,S)                                       645
C                                                                        646
C  THIS ROUTINE CALCULATES EIGENVALUES AND EIGENVECTORS OF THE SCALED    647
C  MATRIX A                                                              648
C                                                                        649
      DIMENSION A(12,12),S(12,12),VAL(12)                                650
      DO 42 I=1,N                                                        651
      DO 43 J=1,N                                                        652
   43 S(I,J)=0.                                                          653
   42 S(I,I)=1.                                                          654
      FN=0.                                                              655
      DO 1 I=2,N                                                         656
      I1=I-1                                                             657
      DO 2 J=1,I1                                                        658
    2 FN=FN+A(I,J)*A(I,J)                                                659
    1 CONTINUE                                                           660
      FN=SQRT(2.*FN)                                                     661
      UN=FN*1.E-9                                                        662
      PN=N                                                               663
    3 FN=FN/PN                                                           664
    8 IN=0                                                               665
      DO 24 IQ=2,N                                                       666
      L=IQ-1                                                             667
      DO 22 IP=1,L                                                       668
      IF(ABS(A(IP,IQ)).LE.FN) GOTO 22                                    669
      IN=1                                                               670
      V=-A(IP,IQ)                                                        671
      U=.5*(A(IP,IP)-A(IQ,IQ))                                           672
      W=SIGN(1.,U)*(V/SQRT(V*V+U*U))                                     673
      DET=1.-W*W                                                         674
      SN=W/SQRT(2.*(1.+SQRT(DET)))                                       675
      CN=SQRT(1.-SN*SN)                                                  676
      DO 15 I=1,N                                                        677
      BIP=A(I,IP)*CN-A(I,IQ)*SN                                          678
      BIQ=A(I,IP)*SN+A(I,IQ)*CN                                          679
      A(I,IP)=BIP                                                        680
      A(I,IQ)=BIQ                                                        681
      BIP=S(I,IP)*CN-S(I,IQ)*SN                                          682
      BIQ=S(I,IP)*SN+S(I,IQ)*CN                                          683
      S(I,IP)=BIP                                                        684
   15 S(I,IQ)=BIQ                                                        685
      BIP=A(IP,IP)*CN-A(IQ,IP)*SN                                        686
      BIQ=A(IP,IQ)*SN+A(IQ,IQ)*CN                                        687
      BPQ=A(IP,IQ)*CN-A(IQ,IQ)*SN                                        688
      BQP=A(IP,IP)*SN+A(IQ,IP)*CN                                        689
      A(IP,IP)=BIP                                                       690
      A(IQ,IQ)=BIQ                                                       691
      A(IP,IQ)=BPQ                                                       692
      A(IQ,IP)=BQP                                                       693
      DO 20 I=1,N                                                        694
      A(IP,I)=A(I,IP)                                                    695
   20 A(IQ,I)=A(I,IQ)                                                    696
   22 CONTINUE                                                           697
   24 CONTINUE                                                           698
      IF(IN.EQ.1) GOTO 8                                                 699
      IF(FN.GT.UN) GOTO 3                                                700
      N1=N-1                                                             701
      DO 30 K=1,N1                                                       702
      L=0                                                                703
      BIGA=A(K,K)                                                        704
      K1=K+1                                                             705
      DO 31 J=K1,N                                                       706
      IF(BIGA.GE.A(J,J)) GOTO 31                                         707
      BIGA=A(J,J)                                                        708
      L=J                                                                709
   31 CONTINUE                                                           710
      IF(L.EQ.0) GOTO 30                                                 711
      A(L,L)=A(K,K)                                                      712
      A(K,K)=BIGA                                                        713
      DO 35 I=1,N                                                        714
      SB=S(I,L)                                                          715
      S(I,L)=S(I,K)                                                      716
   35 S(I,K)=SB                                                          717
```

```
      30 CONTINUE                                                          718
         DO 50 I=1,N                                                       719
      50 VAL(I)=A(I,I)                                                     720
         RETURN                                                            721
         END                                                               722
         SUBROUTINE MIAVA(N,VAL,VEC,BAST,XAST,DIAG)                        723
C                                                                          724
C  THIS ROUTINE CALCULATES THE SCALED SHIFTS                               725
C                                                                          726
         DIMENSION VAL(12),VEC(12,12),BAST(12),XAST(12),DIAG(12)           727
         DO 1 I=1,N                                                        728
         IF(ABS(VAL(I)).LE.1.E-6) VAL(I)=1.                                729
       1 CONTINUE                                                          730
         DO 4 I=1,N                                                        731
         XAST(I)=0.                                                        732
         DO 2 J=1,N                                                        733
         S=0.                                                              734
         DO 3 K=1,N                                                        735
       3 S=S+VEC(I,K)*VEC(J,K)/ABS(VAL(K))                                 736
         IF(I.EQ.J) DIAG(I)=S                                              737
       2 XAST(I)=XAST(I)+S*BAST(J)                                         738
       4 CONTINUE                                                          739
         RETURN                                                            740
         END                                                               741
```

Example 1. Titration of a weak acid with a weak base. Titrand: 0.6060*M* acetic acid (15 ml + 95 ml of 0.16*M* $NaClO_4$; dilution factor 0.13636). Titrant: 5.081*M* pyridine (input value 5). Parameters to be refined (*i*) E° (EO), (*ii*) concentration of titrant (i.e. pyridine) (CTL2), (*iii*) log K_1^H for acetic acid (K11), (*iv*) log K_1^H for pyridine (K21).

Input

```
   PYRIDINE-CH3COOH I=0.15(NACLO4)
99 2 4E0   CTL2 K11   K21
4.60
5.30
25.        -13.69
   PYRIDINE-CH3COOH I=0.15(NACLO4)
0.         0.         110.    440.    0.      0.
0.60597    0.          1 0 0.13636
0.         5.          0 0 0.

0.21   227.0  00.50   201.8  00.80   185.9  01.00   177.8  01.20   170.6  0
1.50   161.4  01.80   153.6  02.09   147.1  02.45   140.3  02.80   134.8  0
3.32   128.2  03.90   122.2  04.40   117.9  04.85   114.5  1
```

Output

```
          PYRIDINE-CH3COOH I=0.15(NACLO4)
LOG.K11=   4.600
LOG.K21=   5.300

    TEMPERATURE=   25.000
    SL=   59.159
    KWL= -13.690

TITRATION  1        PYRIDINE-CH3COOH I=0.15(NACLO4)
     COH = 0.            FDILH= 0.          CTH = 0.           V0= 110.000   E0= 440.000   JA=   0.
     COL1= 0.60597000    FDIL1= 0.13636000  CTL1= 0.           NP01= 1   NPT1= 0
     COL2= 0.            FDIL2= 0.          CTL2= 5.00000000   NP02= 0   NPT2= 0

     NO. OF POINTS  14

TOTAL NO. OF POINTS  14

ST.DEV.= 0.414E 00     R(HAMILTON)= 0.133E 00     WITH THE INPUT DATA

CYCLE N.  4       ST.DEV.= 0.471E-02     R(HAMILTON)= 0.152E-02

                        VALUE              ST.DEV.
                EO     442.8560295      0.1335093E 00
                CTL2     5.0778247      0.4476654E-01
                K11      4.5174921      0.4945248E-02
                K21      5.2582256      0.2922945E-02

        V       DV       E      PH     Z1     Z2
1   0.2100 0.0036  227.00  3.649  0.881  0.976
    0.5000 0.0037  201.80  4.075  0.735  0.938
    0.8000 0.0043  185.90  4.343  0.599  0.892
    1.0000-0.0011  177.80  4.480  0.521  0.857
    1.2000-0.0020  170.60  4.602  0.451  0.819
    1.5000-0.0054  161.40  4.758  0.365  0.760
    1.8000-0.0065  153.60  4.889  0.298  0.700
    2.0900-0.0026  147.10  4.999  0.248  0.645
    2.4500 0.0037  140.30  5.114  0.202  0.582
    2.8000 0.0078  134.80  5.207  0.170  0.529
    3.3200 0.0027  128.20  5.319  0.136  0.465
    3.9000 0.0010  122.20  5.420  0.111  0.408
    4.4000-0.0027  117.90  5.493  0.096  0.368
    4.8500-0.0020  114.50  5.550  0.085  0.338
```

Example 2. Titration of a mixture of weak bases with a strong acid. Titrand: 1.543m*M* pyridine + 1.872m*M* 2,2'-bipyridyl (input values 1 and 2). Titrant: 0.0997*M* $HClO_4$. Parameters to be refined (*i*) E° (EO), (*ii*) concentration of pyridine (COL1), (*iii*) concentration of 2,2'-bipyridyl (COL2). In the output, *Zi* is equal to the average number of protons bound to the ligand *i*.

Input

```
   PYRIDINE-2,2-BIPYRIDYL I=0.1(NACLO4)
99 2 3EO    COL1 COL2
5.33
4.461
25.         -13.75
   PYRIDINE-2,2-BIPYRIDYL I=0.1(NACLO4)
0.          0.0997     100.    420.    -480.  0.
0.001       0.           0 0 0.
0.002       0.           0 0 0.

0.05   8.60   00.15   38.30  00.25   53.00  00.35   63.00  00.45   71.00  0
0.60   80.60  00.75   88.90  00.90   96.10  01.04   102.2  01.15   106.7  0
1.30   113.0  01.50   120.5  01.65   126.4  01.80   132.1  02.00   139.2  0
2.15   144.9  02.30   150.5  02.46   156.9  02.65   164.4  02.81   171.6  0
2.99   179.8  03.12   186.4  03.25   193.3  03.45   203.9  03.56   209.6  0
3.70   216.1  03.85   221.9  04.00   227.2  04.15   231.8  04.40   238.0  1
```

Output

```
            PYRIDINE-2,2-BIPYRIDYL I=0.1(NACLO4)
LOG.K11=    5.330
LOG.K21=    4.461

    TEMPERATURE=    25.000
    SL=    59.159
    KWL= -13.750

TITRATION  1          PYRIDINE-2,2-BIPYRIDYL I=0.1(NACLO4)
     COH = 0.              FDILH= 0.             CTH = 0.09970000    VO= 100.000    EO= 420.000    JA=-480.000
     COL1= 0.00100000      FDIL1= 1.00000000     CTL1= 0.            NPO1= 0    NPT1= 0
     COL2= 0.00200000      FDIL2= 1.00000000     CTL2= 0.            NPO2= 0    NPT2= 0

     NO. OF POINTS  30

TOTAL NO. OF POINTS  30

ST.DEV.= 0.456E 00      R(HAMILTON)= 0.175E 00      WITH THE INPUT DATA

CYCLE N.  6        ST.DEV.= 0.244E-02      R(HAMILTON)= 0.935E-03

                          VALUE              ST.DEV.
                EO       415.9951820        0.7832945E-01
                COL1       0.0015484        0.3835969E-05
                COL2       0.0018658        0.2824248E-05

          V       DV       E       PH      Z1      Z2
   1   0.0500-0.0010     8.60   6.886   0.027   0.004
       0.1500-0.0017    38.30   6.384   0.081   0.012
       0.2500-0.0006    53.00   6.136   0.135   0.021
       0.3500-0.0011    63.00   5.967   0.187   0.030
       0.4500-0.0000    71.00   5.832   0.240   0.041
       0.6000-0.0011    80.60   5.669   0.314   0.058
       0.7500 0.0020    88.90   5.529   0.387   0.079
       0.9000 0.0017    96.10   5.407   0.456   0.102
       1.0400-0.0006   102.20   5.304   0.515   0.125
       1.1500-0.0036   106.70   5.228   0.558   0.146
       1.3000 0.0025   113.00   5.122   0.618   0.179
       1.5000-0.0040   120.50   4.995   0.684   0.226
       1.6500 0.0023   126.40   4.895   0.731   0.269
       1.8000 0.0054   132.10   4.799   0.773   0.315
       2.0000-0.0029   139.20   4.679   0.818   0.377
       2.1500 0.0003   144.90   4.582   0.848   0.431
       2.3000-0.0016   150.50   4.488   0.874   0.485
       2.4600 0.0030   156.90   4.379   0.899   0.547
       2.6500-0.0030   164.40   4.252   0.923   0.618
       2.8100 0.0026   171.60   4.131   0.941   0.682
       2.9900-0.0026   179.80   3.992   0.956   0.747
       3.1200-0.0013   186.40   3.880   0.966   0.792
       3.2500-0.0002   193.30   3.763   0.974   0.833
       3.4500-0.0007   203.90   3.583   0.982   0.883
       3.5600 0.0023   209.60   3.486   0.986   0.904
       3.7000 0.0035   216.10   3.376   0.989   0.924
       3.8500-0.0032   221.90   3.277   0.991   0.939
       4.0000-0.0014   227.20   3.186   0.993   0.950
       4.1500 0.0018   231.80   3.107   0.994   0.958
       4.4000-0.0002   238.00   3.001   0.995   0.967
```

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DETERMINATION SPECTROPHOTOMETRIQUE DES CONSTANTES D'ACIDITE DE QUELQUES 2,1,3-BENZOSELENADIAZOLES (PIAZSELENOLES)

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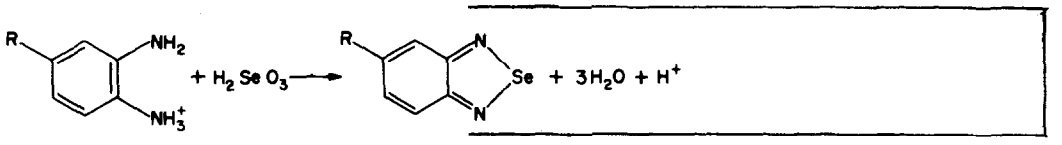
Résumé—Après avoir étudié les spectres d'absorption dans l'ultraviolet et le visible du 2,1,3-benzosélénadiazole et de cinq de ses dérivés en fonction de l'acidité du milieu réactionnel, on a déterminé les valeurs de leurs constantes d'acidité en faisant usage d'une méthode numérique qui permet de corriger les effets de milieu. Les résultats d'une étude spectroscopique infrarouge de ces mêmes dérivés ainsi que de leurs orthodiamines correspondantes ont été corrélés aux pK_a ainsi qu'à la somme des constantes de substitution $\sigma_m + \sigma_p$ de Hammett.

La détermination quantitative du sélénium fait le plus souvent appel à la réaction, en milieu acide, entre le sélénium(IV) et une orthodiamine aromatique.[1–6] Dans ces conditions, il se forme un benzosélénadiazole, plus communément appelé piazsélénole, dérivé soluble dans divers solvants organiques:



Parmi les orthodiamines, le 1,2-diaminobenzène et ses dérivés substitués (4-méthyl, 4-chloro, 4-nitro et 4,5-dichloro) ainsi que le 2,3-diaminonaphtalène sont les plus utilisés.

Les piazsélénoles ainsi obtenus ont déjà fait l'objet de plusieurs études. Certains chercheurs ont notamment montré qu'un acide fort ajouté aux solutions aqueuses de ces composés provoque un déplacement spectral bathochrome accompagné parfois d'un effet hyperchrome.[7–10] Approfondissant ce phénomène, Sawicki et Carr[11–13] mirent en évidence, en particulier pour les dérivés 2,1,3-benzosélénadiazoles substitués en 5, une protonation des deux azotes tertiaires de la molécule ainsi que des différences spectrales entre les formes basique, monoprotonée et diprotonée.

Ces faits nous ont incités à procéder à la détermination précise, par spectrophotométrie, des constantes d'acidité des principaux dérivés séléniés du type piazsélénole. La protonation complète de ces dérivés à caractère basique très faible a nécessité l'usage de fortes acidités (jusqu'a 96% d'acide sulfurique); dans ces conditions, en raison de l'effet de changement de solvant, il est normal de constater des déplacements spectraux, parfois importants, par rapport aux points isosbestiques, faussant toute mesure d'absorption, en particulier celle de l'espèce protonée, et rendant par conséquent incorrecte toute détermination des pK_a. C'est afin de pallier cet inconvénient que nous utilisons une méthode numérique originale, mise au point récemment.[14,15]

En outre, nous avons pu établir une corrélation entre, d'une part, les pK_a ainsi obtenus et les pK_a des orthodiamines, déterminés lors d'un travail antérieur,[16] et, d'autre part, certains paramètres de leur spectre infrarouge.

PARTIE EXPERIMENTALE

Appareillage

Spectrophotomètres Beckman Acta V avec cellules de quartz de 1 cm et Perkin–Elmer 177 avec cuvettes à fenêtres en NaCl.

Réactifs

Dichlorométhane (Merck P. A.) désséché sur tamis moléculaire Merck 3 Å.

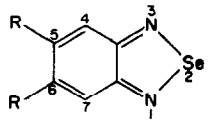
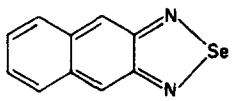
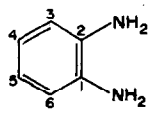
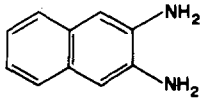
Acide sélénieux (Baker Analyzed Reagent).

La structure chimique des produits étudiés ainsi que la nomenclature utilisée, sont rassemblés au tableau 1.

Synthèse et purification

Les piazsélénoles sont préparés par mélange d'une solution dans l'acide chlorhydrique 1*N* d'une orthodiamine (purifiée selon une technique décrite précédemment[16]) à un même volume d'une solution aqueuse contenant une quantité équimoléculaire d'acide sélénieux. Le précipité est recueilli et lavé à l'aide d'acide chlorhydrique 0,01*N*, puis d'eau distillée, et ensuite séché sous vide, à température ordinaire. La purification est réalisée par sublimation sous un vide d'environ 1 mmHg, à une température de 35 à 110° selon le composé (tableau 2); un seul dérivé, sensible à la temperature, le naphtosélénadiazole, a été purifié par précipitation par ajoute d'eau distillée à sa solution éthanolique saturée.

Tableau 1. Structure des dérivés étudiés

	R_5	R_6	
	H	H	2,1,3-benzosélénadiazole ou piazsélénole PIS
	CH_3	H	5-CH_3-PIS
	Cl	H	5-Cl-PIS
	NO_2	H	5-NO_2-PIS
	Cl	Cl	5,6-diCl-PIS
	—	—	2,1,3-naphtosélénadiazole ou 5,6-benzo-PIS
	R_4	R_5	
	H	H	1,2-diaminobenzène ou orthophénylènediamine PD
	CH_3	H	4-CH_3-PD
	Cl	H	4-Cl-PD
	NO_2	H	4-NO_2-PD
	Cl	Cl	4,5-diCl-PD
	—	—	2,3-diaminonaphtalène ou 4,5-benzo-PD

Ces piazsélénoles, conservés en chambre froide, en récipients fermés, sont stables pendant plusieurs mois, à l'exception du naphtosélénadiazole qui se dégrade rapidement et ne peut, dès lors, être manipulé que fraîchement préparé.

Les points de fusion déterminés à l'aide d'un microscope à platine chauffante, figurent au tableau 2.

Mode opératoire

Après avoir préparé des solutions d'acide sulfurique (5 à 96% p/p), on en détermine la densité. La valeur correspondante de H_0 (Hammett) est interpolée à partir de ces résultats et des valeurs publiées.[18]

D'autre part, 5 ml d'une solution méthanolique de piazsélénole ($4.10^{-4}M$) sont introduits dans un ballon jaugé de 50 ml; le solvant est évaporé à 30° et le résidu est dissous, soit dans de l'eau distillée, soit dans l'une des solutions acides et on complète au volume avec le même liquide. En raison de l'instabilité du naphtosélénadiazole en milieu acide dilué dès la moindre élévation de température, les résidus provenant de l'évaporation sont dissous dans une quantité connue d'acide sulfurique à 44% (à cette acidité, la redissolution ne nécessite pas de chauffage) et la solution est amenée à 50 ml à l'aide d'eau distillée. (La détermination de la densité des solutions d'acide sulfurique à 44%, diluées dans les mêmes conditions, permet de connaître la concentration des solutions ainsi obtenues.)

L'absorption de chaque solution est mesurée à une longueur d'onde adéquate par rapport au réactif blanc.

Toutes les déterminations ont été effectuées à 25 ± 1°.

Si A_M et A_I représentent respectivement les absorptions des espèces moléculaire et ionique ($A_I > A_M$) et si A correspond à un mélange des deux espèces en équilibre, variable selon l'acidité du milieu (H_0), le pK_a est donné par la relation:

$$pK_a = H_0 + \log \frac{A - A_M}{A_I - A}.$$

RESULTATS ET DISCUSSION

Etude spectroscopique ultraviolet/visible en fonction de l'acidité

L'incorporation de sélénium à une orthodiamine entraîne l'apparition, dans le spectre d'une bande d'absorption très intense située à la limite de la zone visible et attribuable à deux absorptions du type $\pi \rightarrow \pi^*$.[19] Le tableau 3 précise la localisation de cette bande pour les formes dibasique, monoprotonée et diprotonée, ainsi que la valeur des coefficients d'absorption molaire (ϵ) calculés aux maxima d'absorption: y figurent en outre, la longueur d'onde des différents points isosbestiques observés pour les transitions correspondant aux deux ionisations, ainsi que

Tableau 2. Propriétés physiques des dérivés séléniés

Dérivé	Coloration	Température de sublimation, °C*	Points de fusion, °C	Points de fusion, °C[11,17]
PIS	Blanc	35	73–74	73–74
5-CH_3-PIS	Blanc	55	69–70,5	72–73,5
5-Cl-PIS	Jaune pâle	60	120	118–121
5-NO_2-PIS	Jaune	80	220–221,5	220–224
5,6-diCl-PIS	Jaune pâle	110	162–162,5	163–164
5,6-benzo-PIS	Rouge	200†	270†	270†

* Sous un vide de 1 mmHg.
† Avec décomposition.

Tableau 3. Caractéristiques spectrales des solutions aqueuses de piazsélénoles

Dérivé	Bande principale						Points isosbestiques				$[H_2SO_4]$, % p/p, pour formation complète	
	Espèce dibasique		Espèce monoprotonée		Espèce diprotonée							
	λ_{max} nm	ϵ_{max} $l.mole^{-1}.cm^{-1}$	λ_{max} nm	ϵ_{max} $l.mole^{-1}.cm^{-1}$	λ_{max} nm	ϵ_{max} $l.mole^{-1}.cm^{-1}$	pK_{a_1}		pK_{a_2}		Espèce monoprotonée	Espèce diprotonée
PIS	331,5	$1,74.10^4$	341	$1,98.10^4$	362,5	$2,38.10^4$	203 251	231 269	287 379	347	54,5	96
5-CH_3-PIS	335	$1,70.10^4$	348,5	$2,05.10^4$	370	$2,47.10^4$	207 253	236 280	295 387	353	54,5	94
5-Cl-PIS	338	$1,69.10^4$	350	$1,86.10^4$	376	$2,07.10^4$	212 256	240 274	210,5	299	67	96
5-NO_2-PIS	344	$1,65.10^4$	348,5	$1,69.10^4$	—	—	260 310	289 346,5	—	—	70	—
5,6-diCl-PIS	347	$1,93.10^4$	363,5	$2,15.10^4$	400	$1,95.10^4$	211 261,5	249,5 288	213	322	70	96
5,6-benzo-PIS	378,5	$1,82.10^4$	397,5	$1,73.10^4$	404	$1,37.10^4$	263 371 381	333 375,5	204 271 310	241,5 296	54,5	94

Tableau 4. Constantes d'acidité des piazsélénoles (25°C)

Dérivé	pK_{a_1}				pK_{a_2}				Observations
	λ*	pK_{a_1}	n†	s§	λ*	pK_{a_2}	n†	s§	
PIS	341	−1,41	35	0,02	362	−8,10	14	0,02	Effet de milieu pour pK_{a_1} et pK_{a_2}
5-CH_3-PIS	348,5	−1,07	13	0.03	370	−7,55	14	0,02	Effet de milieu pour pK_{a_1} et pK_{a_2}
5-Cl-PIS	350	−2,01	15	0,01	377,5	−8,66	16	0,01	Effet de milieu pour pK_{a_1} et pK_{a_2}
5-NO_2-PIS	245	−2,78	37	0,03	—	—	—	—	Effet de milieu pour pK_{a_1}
5,6-diCl-PIS	363,5	−2,57	12	0.02	400	−9,03	16	0.01	Effet de milieu pour pK_{a_1} et pK_{a_2}
5,6-benzo-PIS	397,5	−1,30	15	0,02	440	−7,78	16	0,02	Effet de milieu pour pK_{a_2}

* Longueur d'onde (nm) à laquelle les mesures ont été effectuées.
† Nombre d'essais.
§ Déviation standard calculée à partir des antilogarithmes.

la concentration d'acide nécessaire pour protoner totalement les différents dérivés. L'analyse de ce tableau met également en évidence l'effet classique[11–13,20] "donneur d'électrons" des substituants sur la localisation de la bande d'absorption principale; on constate aussi que les protonations successives des amines entraînent des déplacements bathochromes.

Determination des constantes d'acidité

Pour le piazsélénole et ses dérivés 5-méthyl, 5-chloro et 5,6-dichloro, on décèle un léger effet de milieu qui se manifeste par un déplacement des tracés spectraux au niveau d'un point isosbestique situé, selon les cas, entre 335 et 355 nm.

Nous avons toutefois pu, et avec une excellente précision, obtenir les valeurs exactes des constantes d'acidité en utilisant une méthode numérique mise au point antérieurement,[14–16] basée sur la résolution d'un système d'équations à deux inconnues (pK_a, A_I):

$$A = \frac{A_M + A_I\, 10^{(pK_a - H_0)}}{1 + 10^{(pK_a - H_0)}}.$$

Dans cette relation, A_M et A_I représentent respectivement, dans le cas de la détermination du pK_{a_1}, les absorptions des espèces dibasique et monoprotonée et, dans le cas de la détermination du pK_{a_2}, des espèces monoprotonée et diprotonée. Dans tous les cas, A est l'absorption du mélange des deux espèces en équilibre, variable selon l'acidité du milieu réactionnel. H_0 est la valeur de la fonction d'acidité de Hammett.[18] Les résultats figurent au tableau 4.

La méthode permet, en outre, de déterminer l'acidité pour laquelle se manifeste le premier effet de solvant.

L'effet de changement de milieu s'est manifesté de façon plus intense pour le dérivé 5-nitro. L'analyse des tracés de la figure 1 le démontre à sufisance: si les spectres correspondant à une acidité comprise entre 0 et 32–38% p/p d'acide sulfurique passent par les différents points isosbestiques (tableau 3), il n'en est plus de même pour des acidités supérieures et l'ensemble des tracés s'avère alors incohérent.

Seules les absorptions relevées à la longueur d'onde choisie (245 nm) et correspondant uniquement aux tracés spectraux passant par les points isosbestiques doivent être prises en considération dans l'algorithme. C'est pourquoi, au cours d'une première série de déterminations, le nombre de points expérimentaux a été forcément limité; aussi la précision atteinte n'a-t-elle été que de l'ordre de 5%. Ce dernier fait nous a incité à introduire, malgré tout, des points expérimentaux supplémentaires correspondant à des acidités comprises entre 32–38% et 49,5% p/p: cette façon de faire a augmenté sensiblement la précision du résultat final jusqu'à atteindre 1%. Il semble donc que, dans ce domaine d'acidité, l'effet de changement de milieu n'affecte pratiquement pas les mesures effec-

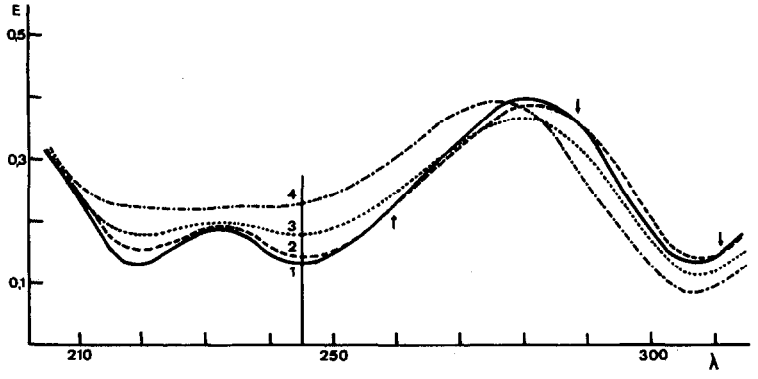


Fig. 1. Etude spectrale du 5-NO_2-PIS en fonction de l'acidité du milieu réactionnel: (1) pH de dissolution, (2) 32% p/p H_2SO_4, (3) 47% p/p H_2SO_4, (4) 64% p/p H_2SO_4.

Tableau 5. Fréquences de vibration infrarouge (cm^{-1}) des orthodiamines aromatiques en solution dans le dichloréméthane

Dérivé	Stretching =C–H aromatique	Stretching C=C cyclique	Stretching N–H asymétrique	Stretching N–H symétrique	Bending N–H scissoring	Bending N–H wagging	Stretching C–N
PD	3065–3032	1595–1501–1458	3425	3348	1623	785	1278
4-CH_3-PD	3070–3014	1596–1517–1450	3422	3346	1628	805	1287
4-Cl-PD	3030	1591–1503–1425	3430	3351	1624	803	1280
4-NO_2-PD	3070*	1593*	3438	3358	1639*	780	1300(?)
4,5-diCl-PD	3052*–3022*	1579–1497	3436	3356	1628	785	1280
4,5-benzo-PD	3050*–3022*	1605*–1586*–1518*–1476*	3432	3352	1642*	785	1281

* Fréquences relevées en pastilles de KBr.

tuées à 245 nm, contrairement à ce que l'étude spectrale laissait supposer.

Remarquons que, pour corriger les effets de changement de milieu, certains auteurs[21,22] préconisent de déplacer latéralement les spectres d'absorption de façon telle que tous passent par le(s) point(s) isosbestique(s). Cette manière de faire suppose donc que l'effet de solvant ne se manifeste que par une simple translation latérale et affecte de la même manière les mesures d'absorption quelle que soit la longueur d'onde. Nous venons de démontrer qu'il n'en est pas toujours ainsi et l'intérêt de la méthode que nous avons mise au point n'en est que plus évident.

Notons encore que la seconde constante d'ionisation du dérivé nitré, à caractère basique beaucoup trop faible, n'a pu être déterminée en milieu acide sulfurique.

Enfin, les graphes de la fonction H_0 en fonction du logarithme du pourcentage d'ionisation sont linéaires; les valeurs absolues des pentes de ces tracés, proches de l'unité, indiquent que la fonction d'acidité choisie[18] s'applique parfaitement à tous les dérivés étudiés.

Etude spectroscopique infrarouge

La plupart des spectres ont été relevés sur des solutions dans le dichloréméthane, seul solvant solubilisant de façon satisfaisante à la fois les orthodiamines sous forme dibasique et les dérivés séléniés correspondants.

Les principaux résultats de l'étude spectrale relative aux diamines aromatiques figurent au tableau 5. L'attribution des bandes caractéristiques a été facilitée en consultant certains résultats partiels trouvés dans la littérature.[23,24] En outre, plusieurs bandes dues aux vibrations de déformation de la liaison C–H en dehors et dans le plan sont observées dans la gamme de fréquences classique, respectivement 650 à 1000 cm^{-1} et 950 à 1225 cm^{-1}. D'autre part, l'attribution pour le dérivé nitré de la bande due au stretching C–N aux environs de 1280 cm^{-1} s'est avérée difficile en raison d'une importante absorption dans cette région, due au radical $-NO_2$ (stretching N=O symétrique). Il est évident que chaque orthodiamine est également caractérisée par la présence de vibrations spécifiques aux divers substituants.

Le tableau 6 rassemble les principaux résultats expérimentaux relatifs aux piazsélénoles étudiés. Comme l'ont constaté Pozdyshev *et al.*,[25] les stretchings =C–H sont légèrement déplacés, par rapport à ceux des diamines libres correspondantes, vers les fréquences plus élevées. Dans la zone d'absorption des liaisons C=C cycliques, de même que l'ont observé Bird et Cheeseman,[26] on note la présence de deux bandes caractéristiques, l'une vers 1610 cm^{-1}, d'intensité variable, et l'autre vers 1505 cm^{-1}, de forte intensité. Une troisième bande apparait aux environs de 1470 cm^{-1}; comme nous le montrerons ci-après, elle pourrait être attribuée à un stretching C=N. Cette bande est d'intensité moyenne pour quatre des dérivés, mais faible pour le naphtosélénadiazole et pour le nitropiazsélénole.

En ce qui concerne ce dernier, cette bande apparaît cependant nettement vers 1440 cm^{-1} sur les spectres

Tableau 6. Fréquences de vibration infrarouge (cm^{-1}) des piazsélénoles en solution dans le dichloréméthane

Dérivé	Stretching =C–H aromatique	Stretching C=C cyclique	Stretching C=N	Stretching cyclique(?)
PIS	3070–3040–3005	1605–1511	1480	1355
5-CH_3-PIS	3063–3040	1626–1509–1451	1490	1350
5-Cl-PIS	3075–3040	1602–1501–1422	1467	1345
5-NO_2-PIS*	3100–3060–3017	1610–1507	1444	1360
5,6-diCl-PIS	3090–3040	1590–1480–1425	1455	1349
5,6-benzo-PIS*	3070–3036	1605–1531–1430	1482	1361

* Fréquences relevées en pastilles de KBr.

relevés sur une dispersion du produit dans le KBr; par contre, elle est difficilement mise en évidence dans le dichloreméthane, en raison de la faible solubilité de ce produit dans le solvant. La comparaison de la position des pics voisins dans le dichloreméthane et le KBr nous a permis, par calcul, d'estimer la position dans le dichloreméthane du pic recherché. Quant au dérivé naphtalénique, la valeur mentionnée au tableau 6 est à prendre avec prudence, le pic correspondant étant de faible intensité dans les deux systèmes.

Il est en outre intéressant de signaler qu'une bande d'intensité moyenne, absente du spectre des orthodiamines libres, apparaît chez tous les piazsélénoles étudiés vers 1350 cm^{-1}; son attribution à un stretching cyclique caractéristique devrait être confirmée.

Tout comme pour les diamines, les vibrations caractéristiques des substituants se retrouvent.

Corrélations entre les constantes d'acidité et les paramètres spectraux

La relation[16] entre les fréquences ν(N–H) (moyenne entre les fréquences symétrique et asymétrique) des orthodiamines étudiées et leur pK_{a_1} est linéaire pour tous les dérivés, mais, lors de l'établissement de la relation entre ν(N–H) et le pK_{a_2}, le composé dichloré et le diaminonaphtalénique s'écartent sensiblement de la droite. Une observation identique est faite lors de l'examen des relations de cette fréquence avec les constantes d'acidité des dérivés séléniés. On peut, de plus, remarquer que le naphtosélénadiazole s'écarte du tracé relatif au pK_{a_1}. Il semble donc que la fréquence ν(N–H) des diamines libres ne soit un paramètre de choix que lors de l'établissement de la corrélation avec le pK_{a_1} des diamines.

Par contre, si l'on fait usage de la fréquence située dans la région 1440–1490 cm^{-1}, on obtient un tracé rectiligne avec les valeurs des pK_{a_1} pour tous les piazsélénoles; cette constatation explique, en partie, la raison pour laquelle nous avons attribué cette vibration à la liaison C=N.

Corrélations entre les constantes de substitution de Hammett et les paramètres spectraux

La relation entre la somme des constantes de substitution de Hammett $(\sigma_m + \sigma_p)$[27] et les fréquences ν(N–H) des orthodiamines et ν(C=N) des dérivés séléniés fournit des tracés rectilignes et les valeurs des carrés des coefficients de corrélation sont proches de l'unité; tel n'est cependant pas le cas si l'on fait usage des valeurs σ_m et σ_p seules.

Enfin, comme l'ont déjà mentionné d'autres auteurs,[28] les fréquences ultraviolettes correspondant aux maxima d'absorption peuvent aussi être reliées aux constantes de substitution, mais la corrélation dans ce cas est nettement moins satisfaisante.

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Summary—The variation with increasing acidity of the ultraviolet/visible region absorption spectrum of 2,1,3-benzoselenadiazole and five of its derivatives has been studied and the ionization constants were determined by using a new computer method for the correction of the medium effect. An infrared spectroscopic study was also done on these derivatives and the corresponding substituted 1.2-diaminobenzenes. Positive correlations were found between some infrared frequencies and either the values of the ionization constants or the sum of the Hammett substitution constants $\sigma_m + \sigma_p$.

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A MICRO CO-PRECIPITATION TECHNIQUE FOR USE IN X-RAY FLUORESCENCE ANALYSIS

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Summary—An apparatus and a procedure are described for the preconcentration of nanogram amounts of trace elements. Co-precipitation and pressure filtration confine the precipitate to a 1.27 mm diameter spot on a filter membrane. Trace elements in the 10–100 ng range are collected reproducibly and detected with high sensitivity by X-ray fluorescence, by use of a milliprobe instrument. Advantages of the technique for quantitative applications are discussed.

Preconcentration of trace elements prior to their determination by X-ray fluorescence affords several significant advantages for practical analyses. By preconcentration and isolation of trace elements on filter paper, interferences from matrix elements have been eliminated, practical standardization procedures have been perfected, and elemental sensitivities of X-ray fluorescence measurements have been greatly improved.[1,2] Several investigators have successfully preconcentrated ng/ml levels of trace elements from large volumes of solution by use of filter papers loaded with ion-exchange resin.[3,4] Although this procedure has been used for semi-quantitative multielement trace analysis of water, several problems are encountered which complicate its application for accurate quantitative measurements. The primary problem of low collection efficiency of trace elements by these loaded papers in the presence of high and variable concentrations of alkali and alkaline earth cations may preclude applications for sea-water analyses. Other problems are that the capacity of the resin paper may be exceeded, and the exchanged trace element may be spread over a fairly large area. Sometimes the same sample is filtered through the same paper, or several filter papers may be used simultaneously. Nevertheless, noteworthy enrichment factors, reasonable precision and linear relationships between concentration and measured X-ray yields have been accomplished and practical applications have been made.[3]

Trace elements have also been preconcentrated by precipitation or co-precipitation prior to collection on filter paper and analysis by X-ray fluorescence.[5–8] In these cases a few μg of various trace elements present either in relatively small volumes of solutions (≤25 ml) or in high purity materials have been determined quantitatively. Other preconcentration steps can be used routinely prior to X-ray analysis. Extraction, evaporation, chelation, adsorption on activated carbon and use of ion-exchange and silylated reagent columns are some of the techniques which can be used where applicable.

Optimization of designs of X-ray spectrometers and improvements in other equipment are obviously important for improving X-ray fluorescence sensitivities for various elements. Construction of specialized X-ray milliprobes will be discussed in a separate paper.[9] X-Ray fluorescence detection limits also depend upon background radiation, matrix element effects, surface topography of samples and sample geometry. The detrimental effects of some of these have been circumvented by using sample collection on filters loaded with ion-exchange resin and composed of elements of low atomic weight.

Confinement of the entire sample to an area equivalent to the size of the milliprobe X-ray beam provides two major advantages. X-Ray fluorescence intensities from trace elements in the sample are increased, and the very small beam leads to limited scatter from the supporting filter. Since X-ray milliprobes have been designed and constructed for microanalysis at this laboratory,[10] it was the objective during the present investigation to perfect a suitable sample-collection procedure providing enhanced X-ray fluorescence detection by means of preconcentration and restriction of sample size to beam dimensions. The present paper reports procedures suitable for the co-precipitation of ng quantities of trace transition elements and the confinement of the precipitate to a 1.27 mm diameter spot on the filter membrane, and these together with the subsequent excitation of fluorescence of the elements by an X-ray milliprobe, provide a method for very sensitive trace analysis ("Coprex").

EXPERIMENTAL

Filtration apparatus

The concept described previously by Luke,[1] of collecting a precipitate on filter paper for subsequent direct X-ray fluorescence determination, has been adopted in the present investigation. The new apparatus for pressure filtration shown in Fig. 1 has several advantages over previous designs based on vacuum filtration.[1,11] The precipitate resulting from treatment of 2 μg of a co-precipitant

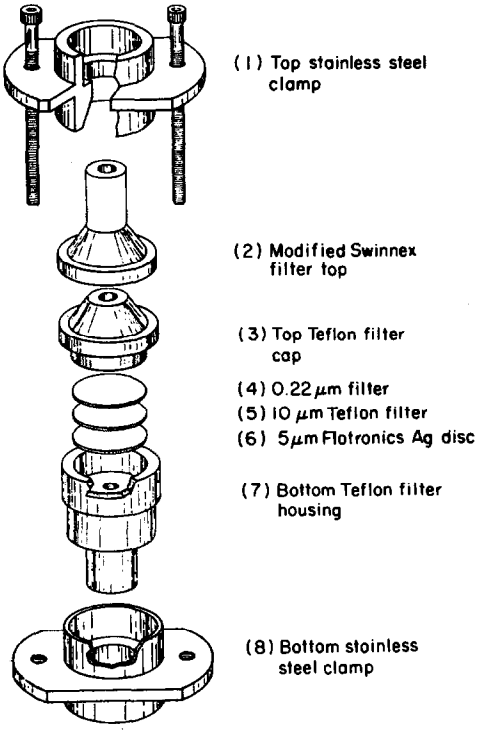

Fig. 1. Teflon filtration unit.

can be collected in an area of 1.27 mm diameter on filter paper. The Teflon filtration unit and corresponding stainless-steel housing are shown in Fig. 1. The bottom section (7) of the unit is loaded successively with a silver membrane to withstand pressure filtration, a Teflon membrane to prevent fusion of the Flotronics membrane to the Millipore cellulose filter pad, and finally, a 0.45 μm Millipore cellulose filter pad on which the precipitate is collected. The filtration unit is then assembled and clamped to prevent leakage. The solution to be filtered is poured into the top of a syringe which is attached by its Luroloc connector to the filtration unit. This assembly is held in the Crescor Lur Ram pressure apparatus (Creative Scientific Equipment Corp., 2305 Cherry Industrial Circle, Long Beach, Cal.). The syringe plunger is inserted and pressure (not more than 2 atm) applied by the piston.

All Teflon and stainless-steel parts were designed and machined at Bell Laboratories.

Filter discs. The collection disc was a cellulose plain white HAWP 025-00, 0.45 μm porosity, 25 mm diameter Millipore filter. The Teflon filter disc was a Millipore LCWP 025-00 10 μm porosity type, 25 mm in diameter.

Silver membrane. A Selas (FM-25) Flotronic silver membrane was used (10 μm porosity, 25 mm diameter) (Ember Products, 4 Taft Road, Totowa, New Jersey, 07512).

Filter unit cap. A Swinnex 25 mm [Fig. 1, (2)] filter holder, Millipore type SX00-025-00, was altered to produce the filter unit top.

Syringe. A 5 ml gas-tight glass Luraloc syringe, model 1005, with a Teflon centre hub and a plunger fitted with a low friction Teflon tip (model 13713) (Hamilton Syringe Co., 4960, Energy Way, P.O. Box 7500, Reno, Nevada 90502).

Reagents

High-purity "Ultrex" perchloric acid (J. T. Baker Chemical) and "Suprapur" ammonia (EM Reagents Division, Brinkmann Instruments, Inc., Westbury, NY 11590) were used. High purity ammonia was also obtained from a gas generator.[12] Aqueous sodium diethyldithiocarbamate solution (2%) was prepared from reagent grade material and filtered through a 0.22 μm porosity Millipore membrane. Standard solutions of Ti^{4+} (10 μg/ml) and of a mixture containing 10 μg/ml each of Cu^{2+}, Ni^{2+}, Fe^{3+}, Co^{2+} and Cr^{3+}, were prepared by diluting concentrated stock solutions with 10% nitric acid.

Procedures

Co-precipitation. An aliquot of the solution containing the mixture of cations (10–150 ng each) is transferred into a 5-ml Teflon beaker, and 0.05 ml of high-purity perchloric acid (5 ml of 70% perchloric acid + 3 ml of water), a solution containing 2 μg of Ti, and 2.5 ml of pure water are added in that order. The pH of the mixture is adjusted to 3.8–4.5 (pH-meter) by addition of high-purity gaseous ammonia. Two drops of the 2% sodium diethyldithiocarbamate solution are added and mixed. Additional ammonia is then added to increase the pH to 8.0–8.2. After standing for 5 min the mixture is transferred into the syringe barrel after removal of the plunger, being rinsed in with 0.5 ml of distilled demineralized water. The solution is then filtered under pressure as described previously.

X-Ray fluorescence measurements. The filter disc together with the precipitate collected in a microdot is dried at low temperature on a hot-plate in a laminar-flow "clean" hood, then centred in an unbacked aluminium holder (0.63-cm diameter opening) and inserted into the sample compartment of a specially designed X-ray milliprobe. The microdot is aligned directly below the primary X-ray beam aperture and 10-sec or 100-sec counts are taken of the K_α lines of the elements to be determined.

RESULTS AND DISCUSSION

Collection and confinement of trace elements to a microspot

Collection of trace elements in a sample by co-precipitation and precise confinement to a 1.27-mm diameter spot has been accomplished by using the pressure-filtration apparatus shown in Fig. 1. This procedure circumvents some problems occurring during preconcentration of trace elements on chelating or ion-exchange resin paper when filtration of large volumes of solution causes collected trace elements to occupy relatively large areas of the filter.[3] In these cases the collection area on the filter is usually larger than the aperture of the filtration apparatus and several times greater than the area of the primary X-ray beam. Sensitivity is thus lost because only a fraction of the collected sample is utilized for generating fluorescence X-rays.

A pressure filtration was adopted since vacuum techniques could not be used successfully for filtering even small volumes ($\leq$5 ml) of solutions through fine porosity Millipore filters. The Teflon filter fixture and housing (Fig. 1) can be connected to a suitable syringe, and the commercially available Lur Ram device was used to provide controlled pressure to the plunger of the syringe. Examination of various syringes indicated that a 5-ml glass, gas-tight Luraloc syringe with a Teflon centre hub was most efficient. The plunger of the syringe was fitted with a Teflon tip which formed a sliding seal with the interior of

Table 1. The pH-dependence of recovery of elements co-precipitated as diethyldithiocarbamates

pH	X-Ray intensity, *cps**						
	Cu	Ni	Co	Fe	Mn	Cr	Ti
2.8	3410	4681	3923	3313	1072	1867	7935
3.0	3623	4721	4024	3313	1517	1930	6962
3.5	3627	4970	4189	3503	2022	1927	7142
4.2	3594	4965	4117	3557	2139	1953	7542

* 0.2 μg of each element, time of counting 10 sec.

the wall syringe without causing sufficient friction to require more than 2 atm pressure.

Samples are filtered and confined to a 1.27-mm diameter spot consistently, provided that the aperture in the top of the filter housing [Fig. 1, (3)] is 1.27 mm in diameter and that at the bottom is restricted to 1.00 mm [Fig. 1, (7)]. The efficiency and time of filtration are dependent on the porosity of the cellulose filter pad. The 0.45-μm type filter gave the optimum collection efficiency and filtration time.

Co-precipitation of trace elements

Microgram amounts of transition elements can be precipitated quantitatively in the pH range 4–9 as dithiocarbamates and hydroxides.[1] Co-precipitation of ng amounts of transition elements from basic solutions containing diethyldithiocarbamate has been examined during the present study. The data reported in Table 1 were obtained by using Ti^{4+} to co-precipitate trace elements from several samples initially containing 25–150 ng of each trace element. The initial pH of each sample was adjusted to a selected value prior to addition of the precipitant solution. No attempt was made to control the final pH of the filtered mixture.

The data in Table 1 show that a constant amount of trace element is recovered when the initial pH is between 3.5 and 4.2. The pH of each solution increases to approximately 5.2 upon addition of the diethyldithiocarbamate reagent. If the initial pH value is above 4.2 the collection efficiency for the diethyldithiocarbamates of certain elements is reduced. Reduced collection efficiency from solutions with pH below 3.5 probably results from the effect of rapid decomposition of the sodium salt of diethyldithiocarbamate and the reduced stability of the metal chelate.

The precipitation of trace elements as hydroxides is shown in Table 2. Adjustment of the pH to 7.2 with ammonia gave results comparable to those obtained with sodium hydroxide at pH 9.0. At pH >9.0 recoveries were higher with sodium hydroxide than with ammonia, particularly for Mn, Co and Ni. Nevertheless, ammonia is the preferred reagent, since it is available in ultrahigh purity grades and can easily be generated in a pure state.

For routine co-precipitation of trace elements the following general procedure was adopted. The initial pH of the sample solution is adjusted to 3.5–4.2 and the diethyldithiocarbamate reagent added. The final pH of the solution is then increased to 8.0 by addition of ammonia prior to pressure filtration. Thus, the advantage of precipitating the elements as either diethyldithiocarbamates or hydroxides is obtained.

Efficiency and precision of co-precipitation

The precision and magnitude of the recovery of Mn and Co by co-precipitation was examined by comparing X-ray counting of the collected precipitates with γ-ray counting of the initial sample solution, collected precipitate and the filtrate. Mn, the most inefficiently precipitated of the transition elements of interest, was studied with Fe as the co-precipitant. Co was selected as representative of the elements previously found to be suitably co-precipitated with Ti. Recovery data for Mn and Co are reported in Table 3. With Fe as the co-precipitant for Mn, recoveries were independent of the initial quantity of Mn over the range 10–100 ng. In the presence of Ti, a less effective co-precipitant, a definite pattern of increasing recovery with increasing amounts of cobalt is seen. Corresponding recovery data for Mn and Co based on X-ray fluorescence measurements were obtained and compared

Table 2. X-Ray intensities of trace elements co-precipitated as hydroxides

pH	X-Ray intensity, *cps**					
	Cu	Ni	Co	Fe	Mn	Cr
Adjusted with NH_3						
4–6	2977	4797	3928	3264	2081	1708
7.2	2930	4465	3884	3237	1824	1769
9.0	2811	3908	2447	3000	1647	1579
Adjusted with NaOH						
4–6	2767	5040	3965	2841	2215	1527
9	2881	4408	3814	3277	2167	1745
11	2858	4573	3748	3247	2357	1589

* 0.2 μg of each element, net counts for 10 sec (corrected for blank).

Table 3. Recoveries of co-precipitated trace elements

Sample added, *ng*		Yield %*
Mn	10	74 ± 10
	50	83 ± 7
	100	79 ± 1
Co	10	44 ± 2
	20	64 ± 7
	50	72 ± 3
	100	77 ± 3

* Percentage of γ-ray activity of ^{60}Co and ^{54}Mn in the collected precipitate compared to original activity of the sample solution, ± relative standard deviation (4 or 5 separate determinations).

with the data in Table 3 and indicated adequate recoveries with good precision by the co-precipitation technique. The mean net X-ray intensity data (9.5, 11.6 and 10.7 cps/ng) for recovery of 10, 50 and 100 ng of Mn confirm the results from isotope experiments (Table 3) showing that the recovery of this element, co-precipitated with Fe, is essentially independent of the initial level of manganese. In contrast, the data for Co (11.8, 16.5, 19.0 and 19.2 cps/ng) for initial quantities of 10, 20, 50 and 100 ng, respectively, indicate that recovery of this element by co-precipitation with Ti^{4+} is concentration-dependent below the 50-ng level. The new technique shows a fivefold improvement in sensitivity over the previous procedure using samples confined to a 3-mm diameter spot. X-Ray data (K_x cps) for precipitates confined to a 3.0-mm spot were 367, 461, 291, 363, 186 and 157 for 100 ng of Cu, Ni, Co, Fe, Mn and Cr, respectively.[13] Corresponding data for the same quantity of these elements confined to a 1.27-mm spot are 1516, 2404, 1968, 1680, 918 and 852 cps. The dependence of X-ray intensity on concentration was linear for Mn and Co. The combination of extreme sensitivity, reproducible recoveries and good proportionality of X-ray intensity data with concentration are promising advantages of the method for quantitative applications. Detailed investigation of blank problems, examination of other quantitative aspects and direct applications of the technique for quantitative analyses are reported in an accompanying paper.[14]

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SEQUENTIAL TESTING AS AN EFFICIENT SCREENING METHOD FOR INTERFERENCES IN ROUTINE ANALYSIS AS APPLIED TO ATOMIC-ABSORPTION SPECTROMETRY WITH FLAME AND GRAPHITE FURNACE ATOMIZATION

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Summary—Reliable standardization is a serious problem for most analytical methods. In spite of extensive work on interferences, the results are not suited for prediction of gross errors in any particular case. This paper is intended to show the power of sequential testing in practical atomic-absorption spectrometric analyses for the efficient detection of interferences causing changes in sensitivity; this test is carried out by comparing the sensitivity of the standard with the sensitivity for the sample, as determined by the difference between the signals for the spiked and unspiked samples. The simple computations can be carried out instantly and experimentation is terminated as soon as a conclusion can be drawn. The major advantage over the traditional tests lies in the smaller number of independent measurements, requiring less time and sample. Three separate cases are discussed: with the mean sensitivity of the standard known and the deviation expected to occur in one direction only (single-sided alternative hypothesis); with the standard deviation of the determination known and the deviation possibly occurring in both directions (double-sided alternative hypothesis); and with the mean and the standard deviation unknown but estimated during the test (sequential *t*-test). It is shown that assumptions about the normal distribution of the data do not impose serious restrictions in practical AAS work.

Most modern methods of instrumental analysis rely on standardization for quantitation of results. The most important assumption in this respect is that the instrument response is independent of all physical and chemical parameters except the analyte concentration. As has been realized by all researchers involved in analytical chemistry this assumption is rarely met and for a good many of the analytical procedures in use just the opposite—the dependence of the signal on additional factors other than the analyte concentration—seems to be true.

The procedure outlined in this paper has proved to be of great value for rapidly deciding on the importance of interferences; sequential testing of the difference in sensitivities between the sample and the standard provides a powerful tool in routine analysis. This method is exemplified for atomic-absorption spectrometry with flame and graphite-furnace atomization, even though it appears to be equally helpful with a variety of other analytical methods. The following discussion, however, will be confined to atomic-absorption spectrometric methods.

From the very beginning of atomic-absorption spectrometry numerous sources of signal bias have been observed, which can be classified according to the suspected or proved mechanism of the effect.[1,2] Almost all interferences are very sensitive to experimental parameters, and this fact has been widely used to reduce specific interferences: changing the instrument design can improve the instrument performance considerably. Even with such instruments available, however, the validity of the data produced has to be judged by the analyst and this can be a burdensome task if a reference method is not readily available. In graphite-furnace atomic-absorption spectrometry where spurious signals are frequently observed from complex matrices, the situation is altogether more complicated.[3] Even if the signal is produced by the analyte itself, deviations from the standard signal are commonplace: it was recently found that interactions between interferents take place in graphite-furnace[4–6] as well as in flame[7] atomization, which amount to a strong interrelationship between groups of interferents and the signal. In spite of our detailed knowledge of interferences in the determination of some elements, the data published to date do not allow a prediction of interferences for samples with varying composition; this situation calls for a decision between "interference present" or "interference absent" for every new sample analysed if certain variations in the matrix composition are expected.

This paper describes the use of different sequential testing procedures for objective decision-making on the basis of differences in sensitivity between the standard signal and the analyte signal of the sample: single-sided and double-sided alternative hypothesis testing is described for determinations with known or unknown random error.

EXPERIMENTAL

Apparatus

A Perkin–Elmer 403 atomic-absorption spectrophotometer with deuterium background-correction; an HGA 72 flameless atomization device with argon as sheath gas (flow-rate 1.5 l./min); a Siemens Kompensograph III recorder, response time 250 or 500 msec for 95% of scale. For flame determination a mixing chamber with a one-slot laminar burner head or a nitrous oxide burner head was used.

Reagents

Stock solutions, metal concentration 1000 ppm, were prepared according to the Perkin–Elmer handbook from analytical grade copper metal, lead nitrate and iron wire. These were dissolved in dilute nitric acid; dilutions of these stock stolutions were prepared daily. All reagents were of analytical grade, unless otherwise stated.

Determination of Cu in serum, with the graphite furnace

Human blood serum was diluted tenfold with distilled water; one portion of this dilution was spiked with copper stock solution so that it contained 1 ng/20 µl more copper than the unspiked sample. The volume change was negligible. One determination of the unspiked and one determination of the spiked sample together constituted one experimental unit. The sample volume was 20 µl per injection (Oxford sampler).

The heating cycle was 30 sec drying at 98°, 60 sec charring at 1000°, 8 sec atomization at 2200° and 10 sec at maximal temperature; an Intensitron hollow-cathode copper lamp was used. The measurement wavelength was 324.8 nm, band-width 0.7 nm, lamp current 20 mA; deuterium background-compensation was used. Peak heights were measured. The mean sensitivity for the standard (expressed in absorbance units per ng) was known to be $0.074 \pm 0.010\ ng^{-1}$.

Determination of Pb in St. Louis dust

A 40–50 mg dust sample, dried at 110° overnight, was heated with 2 ml of conc. nitric acid and 2 ml of conc. hydrofluoric acid (Suprapur) in a PTFE vessel at 160° for 3 hr under pressure; after cooling the solution was transferred to a 100-ml beaker containing approximately 30 ml of saturated boric acid solution at 80°, for about 30 min. After cooling it was transferred to a 50-ml standard flask and made up to volume with distilled water. This procedure is virtually equivalent to those suggested elsewhere.[8–11] The reagent blanks for the digestion solution were negligible. The sample volume per injection was 10 µl of a 21-fold dilution of the sample solution with distilled water.

To perform the test, an aliquot of this dilution was spiked with an additional 2 ng of Pb per 10 µl. In addition, two standard solutions containing 2 and 4 ng/10 µl were prepared. The standard deviation for a determination was found to be 0.009 absorbance unit. The signals for the unspiked sample, the spiked sample and the two standards constituted one experimental unit for paired observations.

An Intensitron hollow-cathode lamp was used. The wavelength for lead was 283.3 nm, band-width 0.7 nm, lamp current 10 mA, deuterium background-compensation. The heating cycle was 30 sec drying at 98°, 60 sec charring at 500°, 5 sec atomization at 2000° and 10 sec at maximal temperature.

Determination of iron in Fly Ash (NBS SRM 1633)

The dissolution procedure was the same as for the St. Louis dust. To avoid dilution steps the iron line at 373.7 nm was used, band-width 0.2 nm, acetylene/air flame (lean) without background-compensation. The Intensitron hollow-cathode lamp was run at 30 mA lamp current.

Two standards containing 25 and 50 ppm of iron were prepared and an aliquot of the sample solution was spiked with an additional 25 ppm of Fe. These three solutions plus the unspiked sample constituted one independent experimental unit; these four solutions were run at random and further sets prepared and run, until a conclusion could be drawn; as depicted in Fig. 4 this required 6 or 11 units, depending on the multiple of the standard deviation it was desired to detect.

As a result of this test it was decided that iron should be determined with the acetylene–nitrous oxide flame with the iron line at 248.8 nm, band-width 0.7 nm.

RESULTS AND DISCUSSION

Sequential testing

Comparative experiments with statistical inference are rather common for the testing of hypotheses in chemical investigations;[12] most of them are performed with a predetermined number of experimental units. As a direct consequence of such a rigid experimental scheme two situations are likely to occur: the difference detected at a chosen level of significance is very large and could have been found with much less experimental effort, or the difference just fails to be significant and further results are needed before a conclusion can be drawn.

When—as is common in analytical chemistry—the observations are obtained one after another, it is generally possible to adopt an alternative procedure in which, as each result becomes available, a simple statistical test is applied to decide whether the results obtained so far indicate a definite conclusion (i.e., acceptance or rejection of a hypothesis), or whether more observations are needed to make the experiment conclusive.[13–15] Experimentation is terminated as soon as a conclusion can be drawn. Therefore, the number of experimental units required is generally smaller than in experiments of predetermined size. This is economically important as it is possible to arrive at a decision with a minimum of time and effort, and this might be of additional value with limited sample sizes. Another important feature of sequential testing is the possibility of obtaining the result that no real difference is to be expected; this result cannot be provided by a testing scheme of predetermined size.

Three separate cases are discussed in this paper.

(*i*) Testing for a difference in mean sensitivity, when the mean sensitivity of the standard is known; in this case, the standard deviations of the sensitivities of the standard and of the sample have to be of equal size.

(*ii*) Testing for a difference in mean sensitivity with paired observations of sample and standard, when the standard deviations of both the mean and the sample sensitivity are known.

(*iii*) Testing for a difference in mean sensitivities with paired observations of sample and standard, when the standard deviations are unknown and may be different in sample and standard.

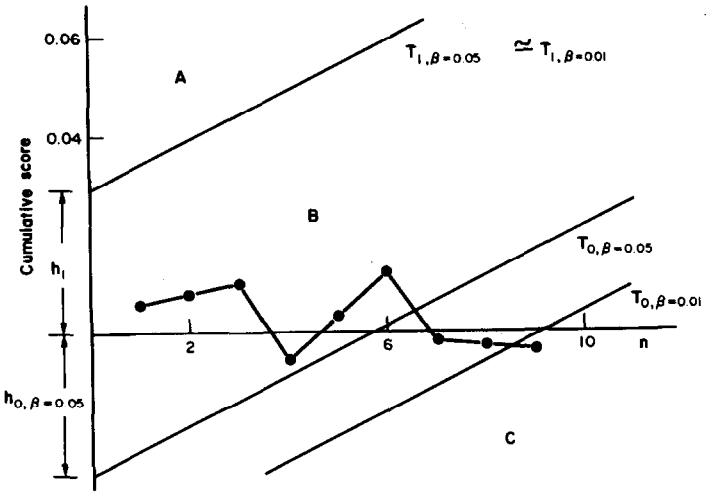

Fig. 1. Single-sided alternative hypothesis for the detection of interferences in the determination of Cu in serum, by using the HGA 72. A—significant decrease in sensitivity; B—no decision; experimentation is continued; C—no real decrease in sensitivity.

Comparison of a mean with a standard value—the single-sided alternative hypothesis

To demonstrate the application of the proposed test to case (i), the determination of copper in serum is chosen, because of previous experience with the determination of copper in other matrices (it has been found that the calibration graph for Cu exhibits practically constant sensitivity even over long periods of time).

To see whether Cu in serum can be determined with a standard calibration graph, the procedure is subjected to a sequential test. Since an *increase* in sensitivity relative to the standard is not expected (analytes in complex matrices tend to give lower sensitivities in graphite-furnace atomization) only a *decrease* in sensitivity is tested for, the alternative hypothesis being that where μ_1 is the mean for the sample, μ_0 the mean for the standard, $\mu_1 < \mu_0$. Before the experiments are carried out several variables have to be fixed which are needed to compute the limits of the inspection scheme. In the following, the quantities are defined as follows: δ is the minimum difference considered significant, α the risk of asserting a significant difference when none exists (error of the first kind), β the risk of asserting no significant difference when the mean value is really $\mu_1 = \mu_0 + \delta$ (error of the second kind), σ the standard deviation.

During the experimentation three situations can be distinguished: (1) in which the alternative hypothesis is accepted; (2) in which there is no decision; (3) in which the null hypothesis is accepted. These are represented by the three zones A, B, and C respectively in Fig. 1. The positions of the two lines T_0 depend on the chosen level of β. The straight lines in Fig. 1 are described by the following equations:

$$T_0 = h_0 + ns = -b\sigma^2/\delta + ns \quad (1)$$

$$T_1 = h_1 + ns = a\sigma^2/\delta + ns \quad (2)$$

where

$$a = \ln(1 - \beta)/\alpha \quad (3)$$

$$b = \ln(1 - \alpha)/\beta \quad (4)$$

$$s = \delta/2 \quad (5)$$

These quantities can be calculated before the experiments are started and laid down graphically, as in Fig. 1, or numerically.

For this example we shall choose $\alpha = \beta = 0.05$ and $\sigma = \delta = 0.010\ \text{ng}^{-1}$.

$a = \ln(1 - 0.05)/0.05 = 2.94$
$b = \ln(1 - 0.05)/0.05 = 2.94$
$s = \delta/2 = 0.005$
$h_0 = -b\sigma^2/\delta = -2.94 \times (0.01)^2/0.01 = -0.029$
$h_1 = a\,\sigma^2/\delta = 2.94 \times (0.01)^2/0.01 = 0.029$
$T_0 = h_0 + ns = -0.029 + 0.005n$
$T_1 = h_1 + ns = 0.029 + 0.005n.$

As the results of the experiments become available they are easily evaluated by simple subtractions; first the signal for the unspiked serum sample is subtracted from the signal for the spiked serum and this sensitivity is subtracted from the standard sensitivity. The score obtained in this way is accumulated until it falls outside the limits set by T_0 and T_1 and the sought-for conclusion can be drawn. For the determination of Cu in serum this is illustrated in Table 1. Inspection of Fig. 1 reveals that the cumulative score crosses the value of T_0 after seven or nine independent experimental units, depending on the chosen level of β. Thus only this number of experiments is needed to show that there is no decrease in sensitivity.

Even though the number of experimental units necessary to arrive at a decision cannot be stated beforehand, it is—in this simple case—possible to calculate an average number of experimental units. This average number $\bar{n}$ is given in Fig. 2 as a function

Table 1. Inspection scheme for interferences in the determination of Cu with the HGA 72

	1	2	3	4	5	6	7	8	9
Serum*	125	131	125	123	133	125	115	128	125
Serum + 1 ng/20 μl*	193	203	197	213	198	190	203	203	200
Sensitivity‡	68	72	72	90	65	65	88	75	75
Score§	+6	+2	+2	−16	+9	+9	−14	−1	−1
Cumulative score	+6	+8	+10	−6	+3	+12	−2	−3	−4

* Signal (absorbance units) × 1000.
† Absorbance units/μg of Cu.
§ The score is calculated as (standard sensitivity − sensitivity); the standard sensitivity is 0.074 ± 0.010 absorbance unit per ng (*i.e.*, ng^{-1}).

of the mean sensitivity; it is evident that the average number required for a conclusion is maximal halfway between the maxima of the density functions. In any event the number of experiments for the sequential test is considerably smaller than for a test of predetermined size.

In spite of the very good demonstrational features of this example, it must be realized that the underlying assumptions can rarely be taken for granted in practical AAS work. It is particularly important to take account of variations in the sensitivity of the standard due to experimental parameters that cannot be controlled satisfactorily. This situation is dealt with in the next section.

Testing for a difference in means among paired observations—the double-sided alternative hypothesis

This is test procedure (*ii*). In contrast to the previous example there are no assumptions made about the sensitivity of the standard.

The model used will be the determination of lead in an aerosol sample. Recent work[6] has indicated that different interferents can cause positive and negative deviations of the lead signal in comparison with the signal of the standard. Therefore, we should test for deviations in both directions: this test is obtained by superimposing two single-sided tests. Some modifications, however, are needed: if the null hypothesis (that there is no effect) is true, there will be two ways an error of the first kind can be made, for it can be wrongly assumed that an increase has occurred or that a decrease has occurred. The definitions of a and b have to be adjusted accordingly:

$$a' = \ln(1 - \beta)/0.5\alpha \quad (6)$$

$$b' = \ln(1 - 0.5\alpha)/\beta \quad (7)$$

The boundary lines are given by the formulae

$$T_0 = h_0 + ns \qquad T_0' = h_0' + ns' \quad (8)$$

$$T_1 = h_1 + ns \qquad T_1' = h_1' + ns' \quad (9)$$

where

$$h_0 = -b'\,\sigma^2/\delta = -h_0' \quad (10)$$

$$h_1 = a'\,\sigma^2/\delta = -h_1' \quad (11)$$

$$s = \delta/2 = -s' \quad (12)$$

Another adjustment is needed for the comparison of means among paired observations; it is related to the standard deviation of the procedure. From previous experience with the determination of lead it is known that the standard deviation of the signals is 0.009; the law of error propagation gives 0.013 for the standard deviation of the sensitivity, calculated for pairs of determinations (each at a different concentration of Pb). Since in this test the score is dependent on two sensitivities, both of them varying independently, the law of error propagation has to be applied for a second time: this gives a total σ of 0.018.

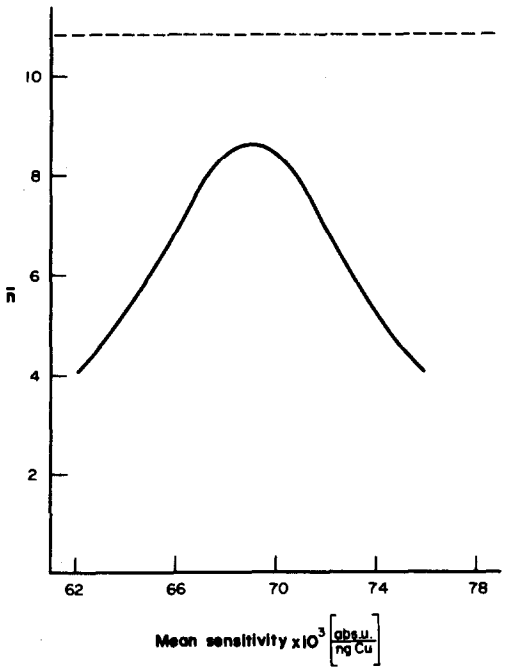

Fig. 2. Average number of experimental units necessary to draw a conclusion; the dotted line gives the number of experimental units required for an experiment of predetermined size.[13]

If $\alpha = \beta = 0.05$ and $\sigma = \delta = 0.018\ ng^{-1}$ are chosen the necessary values are calculated as follows:

$$
\begin{aligned}
a' &= \ln(1-\beta)/0.5\ \alpha \\
&= \ln(1-0.05)/0.025 = 3.64 \\
b' &= \ln(1-0.5\alpha)/\beta \\
&= \ln(1-0.025)/0.05 = 2.97 \\
s &= -s' = 0.009 \\
h_0 &= -h_0' = -2.97 \times (0.018)^2/0.018 = -0.053 \\
h_1 &= -h_1' = 3.64 \times (0.018)^2/0.018 = 0.065 \\
T_0 &= -0.053 + 0.009n \\
T_0' &= 0.053 - 0.009n \\
T_1 &= 0.065 + 0.009n \\
T_1' &= -0.065 - 0.009n.
\end{aligned}
$$

The graphical representation of this experiment is given in Fig. 3. Here again, it is advisable to prepare the test chart before starting the experiments: as the results become available they can be evaluated by a scheme similar to the one shown for copper (Table 1).

In this case the conclusion that there is no real change in sensitivity can be drawn after the seventh comparison, when the cumulative score crosses the line T_0' and thus enters the region C. Consequently, the determination of lead in this dust sample is not seriously biased at the chosen levels of probability.

Testing for a difference in means among paired observations without prior knowledge of the standard deviation

In the sequential tests discussed so far it was assumed that an accurately known value for the standard deviation was available in advance. If the true value of σ were different from the value assumed, then both risks α and β would be different from the values allowed for in the test.

For the determination of iron in the fluoboric–boric acid matrix there is some evidence[16] that silicon and aluminium might cause an interference with the iron signal when atomized in an air–acetylene flame. To check whether this effect or any other interference is of any significance for the determination of iron in environmental dust samples, we run a sequential *t*-test[14] to detect a change in sensitivity, of the magnitude of one standard deviation; the test is planned so that if there is really no difference, that is if $\mu = \mu_0$, the chance would only be $\alpha = 0.05$ that a difference would be found, and that if a change of mean to $\mu = \mu_0 - D\sigma$ occurred, the chance would only be $\beta = 0.05$ that no difference would be found.

After each pair of observations has been made, the deviation $(x_{sample} - x_{standard})$ is noted and the sum

$$T = \Sigma (x_{sample} - x_{standard}) \qquad (13)$$

and the sum of squares

$$S = \Sigma (x_{sample} - x_{standard})^2 \qquad (14)$$

of these deviations are calculated. The function of the observations which is used in the test is

$$U = T/\sqrt{S}. \qquad (15)$$

This quantity U is calculated after each series of measurements and compared with tabulated values of U_0 and U_1.[13] It is noted[13] that the tabulated values are based on a test for an increase of the mean; in testing for a decrease the signs must be reversed or else—as done here—the convention adopted that a difference in the expected direction is always taken as positive. These tables also list the minimum number of experiments necessary to accept or reject the null hypothesis considering the largely indeterminable values of the random error for very small numbers of experiments.

In Fig. 4 U_0 and U_1 are depicted for a deviation equal to the standard deviation ($D = 1$) and a deviation equal to one half of the standard deviation ($D = 0.5$). The values of U found for the determination of iron in Fly Ash (Table 2) permit the conclusive decision after the sixth or the eleventh experimental unit that $\mu = \mu_0 + D\sigma$, depending on the value of D.

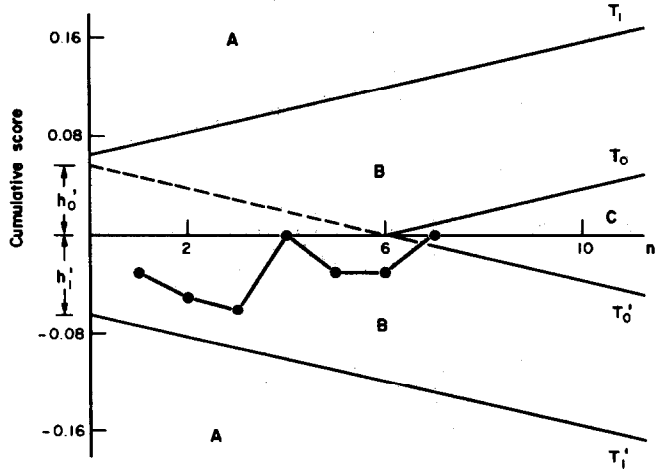

Fig. 3. Double-sided alternative hypothesis of the detection of interferences in the determination of Pb in St. Louis dust. *A*—significant increase or decrease in sensitivity; B—no decision; experimentation is continued; *C*—no real difference from the sensitivity of the Pb standard.

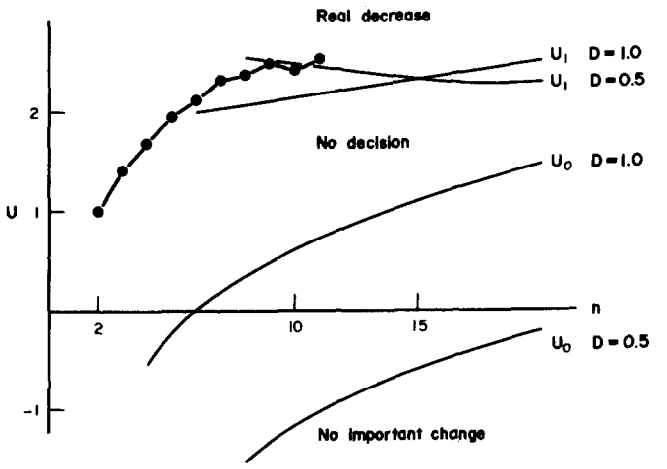

Fig. 4. Sequential t-test for the detection of interferences in the determination of Fe in Fly Ash (SRM 1633) without prior knowledge of the standard deviation. The values for U_0 and U_1 are taken from the appendix in ref. 13.

Table 2. Inspection scheme for interferences in the determination of Fe in Fly Ash with the C_2H_2/air flame

n	1	2	3	4	5	6	7	8	9	10
Standard 1* (25 ppm)	50	54	53	51	52	50	57	55	52	53
Standard 2* (50 ppm)	106	106	107	105	105	106	105	104	100	104
Fly Ash*	104	105	102	104	103	104	103	103	103	102
Fly Ash + 25 ppm*	152	148	151	147	152	149	150	148	152	150
Sensitivity of standard†	56	52	54	54	53	56	48	49	48	51
Sensitivity in Fly Ash†	48	43	49	44	49	45	47	45	50	48
$(x_{sample} - x_{standard})$†	8	9	5	10	4	11	1	4	−2	3
T†	8	17	22	32	36	47	48	52	50	53
S§	64	145	170	270	286	407	408	424	428	437
U‡	1.0	1.41	1.68	1.95	2.13	2.33	2.38	2.53	2.42	2.54

* Absorbance units × 1000.
† Absorbance units/1000 ppm Fe.
§ (Absorbance units/1000 ppm Fe)^2.
‡ Dimensionless.

As predicted by the outcome of the test a direct determination of iron in Fly Ash gives low results (Table 3); a correct result is obtained by the method of standard additions or by the utilization of an acetylene–nitrous oxide flame. A separate test for use of this flame leads to the decision that no difference in sensitivity between sample and standard is to be expected.

CONCLUSIONS

In considering the practical value of the proposed testing procedure some additional remarks are in order. Strictly speaking, a necessary assumption in applying these tests is that the results should be normally distributed; however, moderate deviations from a normal distribution are generally acceptable.[13] If a log–normal distribution is suspected—as frequently

Table 3. Comparison of results for iron in Fly Ash (SRM 1633)

Method	Results, %	95% Confidence limit, %	n
AAS, C_2H_2/air (direct)	4.9	0.2	6
AAS, C_2H_2/air (standard addition)	6.9	1.5*	8†
AAS, C_2H_2/N_2O	6.0	0.4	6
EDXRF[17]	6.2	0.7	6
INAA[18]	6.37	§	§
INAA[19]	6.2	0.3‡	4

* Calculated after Larsen *et al.*[20]
† Number of determinations constituting the standard addition curve.
§ No figure given.
‡ Standard deviation.

claimed for data in trace analysis—a logarithmic transformation will yield the desired normal distribution: this was tried for all the data used here, but did not result in anything but minor deviations from the figures given.

Another important aspect is that the statistical theory asks for "independent measurements"; in practical terms this means that all major sources of variation have to be included. For the determinations in the graphite furnace, for example, the preparation of one or two separate solutions proved to be sufficient, because the major variation in the data stems from the determination itself. In flame atomization the error of pipetting and dilution has to be considered as well; each measurement was done on a separate sample.

If a significant difference in sensitivities is detected the determination cannot be carried out straightforwardly. An alternative is provided by the method of standard additions, if the inherent assumptions [4,7] are fulfilled and the confidence limits associated with this procedure[20] are considered to be narrow enough. Another possibility to get correct results is, of course, to change the experimental parameters sufficiently, as demonstrated by the use of the acetylene–nitrous oxide flame for the determination of iron in Fly Ash.

Although all the examples given are for atomic-absorption spectrometric procedures, it should be emphasized that sequential testing is potentially useful for many, if not all, analytical methods involving standards for quantification of results.

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ANALYTICAL APPLICATIONS OF CONDENSED PHOSPHORIC ACID—II*

DETERMINATION OF ALUMINIUM, IRON AND TITANIUM IN BAUXITES AFTER DECOMPOSITION WITH CONDENSED PHOSPHORIC ACID

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Summary—Bauxites can be decomposed by condensed phosphoric acid (CPA) very rapidly without the need for subsequent manipulations such as elimination of silica, digestion of fused products and filtration. It is best to heat the samples at about 700° prior to the decomposition, to prevent them from floating on the surface of the CPA. Under the proposed conditions (100 mg of sample, 10 g of CPA, heating at 300° for 30 min), aluminium, iron and titanium are dissolved quantitatively. Iron is determined by photometry with 1,10-phenanthroline after solvent extraction with MIBK, while titanium is determined with *N*-benzoyl-*N*-phenylhydroxylamine (BPHA). The effect of phosphate on the determination of titanium is reduced to a minimum at a BPHA concentration of 0.3% and a hydrochloric acid concentration of 7.2*M*. Aluminium and iron are precipitated quantitatively as the oxinates at pH 5.5 in the presence of orthophosphoric acid or hydrolysed CPA, while the precipitation of titanium oxinate is completely suppressed by the addition of hydrogen peroxide. The total amount of aluminium and iron is obtained by determining the amount of oxine by bromination method. The amount of aluminium is obtained by subtracting the amount of iron from the sum of the two.

One of the most difficult problems encountered in the analysis of such refractory oxide minerals as iron ores, chrome ores, bauxites, *etc.* is decomposition of the sample. Although many methods[1–4] have been proposed for the analysis of these materials, they are mainly concerned with the rapid determination of the elements of interest.

Lucas and Ruprecht[5] and Hofton and Baines[6] have reported rapid and simple analytical methods for chrome ores, chrome-magnesite refractories, iron ores and bricks. The samples are dissolved in orthophosphoric acid and the elements determined by atomic-absorption spectrometry. Yamauchi and Otaka[7] and Tamnev *et al.*[8] have also used orthophosphoric acid for decomposing alumina *etc.* before determination of sodium and magnesium.

Faster analysis may be expected if condensed phosphoric acid (CPA) is used instead of orthophosphoric acid. CPA, however, has not been utilized for this purpose except for dissolution of iron ores.[9] This report is concerned with the decomposition of bauxite samples with CPA and the subsequent determination of aluminium, iron and titanium.

EXPERIMENTAL

Reagents

Condensed phosphoric acid (CPA). Prepared as described previously,[9] by heating orthophosphoric acid to the desired temperature. CPA prepared at 280° and 300° will be designated as "280°-CPA" and "300°-CPA", respectively.

Diluted CPA solution (A). Ten g of 300°-CPA diluted to about 50 ml with water and boiled for 15 min, then cooled, and made up to 100 ml with water.

Diluted CPA solution (B). Ten g of 300°-CPA diluted to about 50 ml with water containing 1 ml of concentrated hydrochloric acid and boiled for 15 min, then cooled and made up to 100 ml with water.

The diluted CPA solutions (A) and (B) are 1.1*M* in orthophosphoric acid.

Standard iron(III) solution, 1000 *ppm.* About 4.2 g of ferric alum dissolved in 500 ml of 0.1*M* hydrochloric acid and standardized by addition of excess of EDTA and back-titration with zinc solution (Xylenol Orange as indicator).[10]

Standard titanium(IV) solution, 1000 *ppm.* About 1 g of titanium tetrachloride dissolved in 21 ml of concentrated hydrochloric acid and diluted to 250 ml with water, then standardized as for the iron solution.

Standard thiosulphate solution, 0.1*M*. About 25 g of sodium thiosulphate pentahydrate dissolved in water (previously boiled with 0.2 g of sodium carbonate decahydrate) and diluted to 1 litre with water, then standardized by iodometry, with potassium dichromate as primary standard.

Standard bromine solution, 0.1*N*. About 3.1 g of potassium bromate and 20 g of potassium bromide dissolved in previously boiled and cooled water and diluted to 1 litre with water, then standardized with the standard thiosulphate solution.

Oxine solution, 3%. Three g of oxine dissolved in water containing 10 ml of acetic acid, by heating if necessary, and diluted to 100 ml with water.

1,10-Phenanthroline solution, 0.2%.

N-Benzoyl-N-phenylhydroxylamine (BPHA) solution, 0.3% *in benzene.* This solution must be freshly prepared.

Hydrogen peroxide–ammonia mixture. Ammonia solution (1 + 1) and 2% hydrogen peroxide are mixed in 7:1 volume ratio.

Unless otherwise stated, all chemicals used were analytical-reagent grade. Distilled and demineralized water was used throughout.

* Part I: T. Mizoguchi and H. Ishii, *Talanta*, 1978, **25**, 311.

Samples

Bauxite samples were supplied by the Department of Applied Chemistry, Faculty of Engineering, Tohoku University. They were finely ground in a mortar, dried for 2 hr at 105–110° and then used in the decomposition experiments.

Apparatus

The apparatus used for the decomposition of samples was the same as described previously.[9]

Procedures

Decomposition of bauxites with CPA and preparation of sample solutions. Weight about 0.1 g of the finely powdered sample in a quartz tube. Place the tube on a silica triangle and heat for 2 min at about 700° with a Bunsen burner, cool to room temperature, add 10 g of 280°-CPA and suspend the tube in an electric furnace regulated at 300°. After 30 min, remove the tube from the furnace and cool it to room temperature.

Transfer the reaction mixture into a 100-ml beaker with water, diluting to about 50 ml, then add 1 ml of concentrated hydrochloric acid and heat the solution to boiling. Boil gently for 15 min more, cool to room temperature and then transfer the solution into a 100-ml standard flask. Dilute to the mark with water and use the solution for the determination of aluminium, iron and titanium.

Determination of the degree of decomposition of bauxites. Decompose the insoluble residues in the reaction mixture in the manner described previously.[9] Determine the aluminium and iron in the residue photometrically with oxine.[11] Determine the titanium in the residue photometrically with BPHA as described below. Carry out a blank determination on the reagents and correct the results. Determine the degree of decomposition by the procedure already described.[9]

Titrimetric determination of aluminium with oxine. Take an aliquot of the sample solution, usually 10 ml, in a 100-ml beaker, add 5 ml of 3% oxine solution and dilute to about 70 ml with water. Heat to about 70° and add 4.5 ml of hydrogen peroxide–ammonia mixture, the pH of the resulting solution being *ca.* 6.5. Keep at about 70° for 10 min and then allow to stand for 15 min at room temperature. Filter off the precipitate on a Toyo filter paper No. 5B or equivalent and wash well with about 80 ml of hot water. Dissolve the precipitate into a 200-ml Erlenmeyer flask by dropwise addition of 20 ml of hot hydrochloric acid (1 + 1) and wash with hydrochloric acid (1 + 20) until the filtrate is colourless.

Add 20 ml of orthophosphoric acid to the solution and dilute to about 80 ml with water. Pass nitrogen through the solution for about 5 min to remove the dissolved oxygen, add 15 ml of 0.11*N* bromine solution and stopper the flask. After 1 min, add 0.5 g of potassium iodide and titrate the liberated iodine with 0.1*M* thiosulphate solution, using starch as indicator.

If V_B is the volume of 0.1*M* thiosulphate consumed (ml), the aliquot taken for the determination contains

$$\frac{0.1f(V_B - V_A)}{12} - F \text{ mmole of aluminium}$$

where V_A is the volume of 0.1*M* thiosulphate consumed by the 0.11*N* bromine added, f is the factor of the 0.1*M* thiosulphate and F is the amount of iron contained in the aliquot taken, in mmole.

Photometric determination of iron with 1,10-phenanthroline. Take an aliquot of the sample solution, containing 20–200 μg of iron, in a 50-ml separatory funnel. Add 2 ml of 1*M* sodium sulphate and 8 ml of concentrated hydrochloric acid and dilute to about 20 ml with water. Add 10 ml of methyl isobutyl ketone (MIBK) and extract the chloro-complex of iron by shaking for 1 min. Discard the aqueous layer and wash the organic layer by shaking for 1 min with 15 ml of hydrochloric acid (3 + 4) together with 1 ml of 1*M* sodium sulphate. Discard the aqueous layer and strip the iron complex from the organic layer by shaking for 1 min with 10 ml of water. Collect the aqueous layer in a 50-ml standard flask and repeat the stripping once more. Add 1 ml of 10% hydroxylamine hydrochloride and allow to stand for 20 min to reduce iron(III). Add 2 ml of 1*M* sodium acetate and 5 ml of 0.2% 1,10-phenanthroline solution and dilute to the mark with water. Measure the absorbance at 511 nm, in 10-mm glass cells, against a reagent blank. Construct a calibration curve by use of the standard iron solution.

Photometric determination of titanium with BPHA. Take an aliquot of the sample solution, containing 5–50 μg of titanium, in a 50-ml separatory funnel. Add 18 ml of concentrated hydrochloric acid and dilute to about 30 ml with water. Add 10 ml of 0.3% BPHA solution in benzene and extract the titanium complex by shaking for 3 min. Discard the aqueous layer and collect the organic layer in a 50-ml Erlenmeyer flask containing about 2 g of anhydrous sodium sulphate. Measure the absorbance at 380 nm, in 10-mm glass cells, against a reagent blank. Construct a calibration curve by using the standard titanium solution.

RESULTS AND DISCUSSION

The terms "precipitation or solvent extraction in the presence of CPA" will be used to describe the processes in which the CPA or diluted CPA solution has been used, even when most of the CPA has been hydrolysed by dilution.

Decomposition of bauxites with CPA

It has been shown that aluminium and iron are sufficiently soluble in CPA to give concentrations of at least 20 mg of the metal per 10 g of CPA, *i.e.*, amounts adequate for titrimetry and gravimetry,[9] but the solubility of titanium in CPA has not been determined. When 100 mg of titanium(IV) oxide were heated with 10 g of 280°-CPA according to the recommended procedure, the concentration of titanium found in the reaction mixture was as high as 14 mg/10 g of CPA. Therefore, it may be said that the CPA dissolution method is practicable, at least in respect of solubility, in the determination of aluminium, iron and titanium in bauxites.

The decomposition of five kinds of bauxite was tested under the optimum conditions proposed previously for iron ores.[9] For all except the Ramunia bauxite, part of the sample floated on the surface of the CPA and the decomposition was incomplete (Table 1, column 2). The reason may be that the sample is floated on steam generated on its surface. To solve this problem of floating, which was not observed in the decomposition of iron ores, the bauxite samples were heated prior to the decomposition with CPA. The phenomenon of floating was completely suppressed by this treatment, but a small amount of the sample remained undecomposed in the bottom of the tube even after 30 min, resulting in low recoveries of aluminium for some bauxites, *e.g.*, Ranchi and Malaya (column 4).

Table 1. Effect of dehydration pretreatment on the decomposition of bauxites

Pretreatment of sample	Without pretreatment		Dehydration*			
Preparation temp. of CPA, °C	300	280	300		280	
Decomposition temp. of sample, °C	290	300	290		300	
	Degree of decompn., %					
Bauxites	Al	Al	Al	Al	Fe	Ti
Ranchi (India)	98.1	96.2	99.8	100.0	99.7	99.8
Weipa (Australia)	96.5	99.3	99.9	100.0	99.7	94.3
Sematan (Malaysia)	99.1	99.7	100.0	100.0	99.7	99.9
Malay (Malaysia)	98.0	98.7	99.7	100.0	99.9	99.1
Ramunia (Malaysia)	100.0	100.0	100.0	100.0	99.8	99.7

Sample taken 100 mg, CPA added 10 g, heating time 30 min.
* Heated for 2 min at about 700° with a Bunsen burner.

When the bauxite sample is decomposed with CPA at a temperature higher than the preparation temperature of CPA, it is expected that a certain amount of water, depending on the temperature difference, may be expelled from the reaction mixture and cause convection in the tube. This convection may accelerate the dissolution of the sample. The degree of decomposition was tested with 280°-CPA and a decomposition temperature of 300°. From the results shown in column 5, it is evident that irrespective of the kind of bauxite, 99.9% or more of the aluminium is recovered when the samples are heated prior to the decomposition. On the other hand, untreated bauxites float and give low degrees of decomposition (column 3).

Effect of dehydration temperature of bauxites. Weipa bauxite was heated for 15 min at 300, 350, 400, 600 and 800° and decomposed with CPA according to the recommended procedure. When the dehydration temperature was as low as 300°, a part of the sample floated on the CPA surface and the degree of decomposition was as low as 97.1%. On the other hand, when dehydrated at 350° or higher, the sample never floated and the degree of decomposition was as high as 99.9% or higher. The results of thermogravimetry also indicated that most of the water in the bauxites is removed at 250–350° (Fig. 1). It is evident that bauxites can be dehydrated simply by heating for 2 min with a Bunsen burner, so this method is recommended.

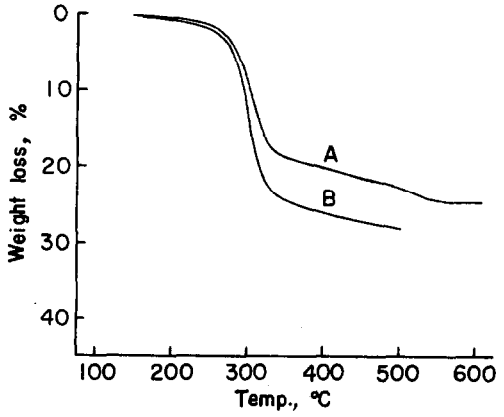

Fig. 1. Thermogravimetric analysis curves for bauxite samples. Sample taken 35 mg, rate of heating 10°/min, standard material α-Al_2O_3. *A*, Ranchi bauxite; *B*, Weipa bauxite.

Effect of heating temperature and time. The degree of decomposition was tested for Weipa bauxite at various temperatures. From the results shown in Table 2, aluminium and iron are easily dissolved in CPA even at 220°, whereas the degree of extraction of titanium is considerably affected by heating temperature in the range 220–320°. Therefore, the decomposition must be continued for 90 min or longer at 300° to obtain 99% recovery of titanium.

A heating temperature of 300° and heating time of 30 min, however, are recommended, in view of the following considerations: (*i*) iron as well as aluminium is completely dissolved in CPA under these condi-

Table 2. Effect of heating temperature and time on the decomposition of bauxites

Heating temp., °C	Heating time, *min*	Degree of decompn., % Al	Fe	Ti
220	30	99.8	98.9	66.2
240	30	99.9	98.9	78.1
260	30	100.0	99.8	85.2
280	30	100.0	99.8	91.3
	10	95.2	85.5	
	15	99.8	97.8	
	20	99.9	98.6	89.7
	25	100.0	99.8	
	30	100.0	99.7	94.3
300	40			97.2
	50			97.9
	60			98.6
	75			98.5
	90			99.2
	120			99.2
320	30	100.0	99.8	97.4

Weipa bauxite was decomposed with CPA according to the recommended procedure. The only difference was that the CPA was prepared at a temperature 20° lower than the decomposition temperature used, *i.e.*, the heating temperature.

tions, (*ii*) CPA may creep up the wall of the tube and solidify there, (*iii*) the degree of decomposition of titanium is as low as 94%, when Weipa bauxite is decomposed by a generally accepted method.[12]

A heating time of 30 min is far shorter than that in the JIS (Japanese Industrial Standard) method,[12] in which bauxites are dissolved with an acid mixture of hydrochloric acid, nitric acid and sulphuric acid by heating for several hours.

Determination of aluminium with oxine

Many chelatometric methods have been proposed for the determination of aluminium in siliceous materials[1,4,13–15] and bauxites.[1,4] These methods, however, require a separation, *e.g.*, by solvent extraction, to eliminate the influence of phosphate. Gravimetry cannot be applied to sample solutions containing CPA because metal ions such as aluminium(III) and iron(III) cannot be precipitated as hydroxides or phosphates by neutralization in the presence of CPA.

On the other hand, precipitation of aluminium oxinate and determination of the oxine by bromination can be performed with satisfactory accuracy even in the presence of CPA. The effect of orthophosphoric acid and CPA on the precipitation of aluminium oxinate is shown by the solid lines in Fig. 2. The minimum pH for quantitative precipitation of aluminium oxinate is 5.5 in both the presence and absence of orthophosphoric acid. The precipitation starts at pH 3.4 in the absence of phosphoric acid, and 4.5 in its presence. Figure 2 also shows that aluminium is precipitated quantitatively at pH > 7 when diluted CPA solution (A) is added. On the other hand, when diluted CPA solution (B) is added, the precipitation behaviour of aluminium is identical with that observed in the presence of orthophosphoric acid. This probably means that almost all of the condensed phosphates are hydrolysed by boiling for 15 min with hydrochloric acid. This hydrolysis is necessary for the analysis of bauxites (see below).

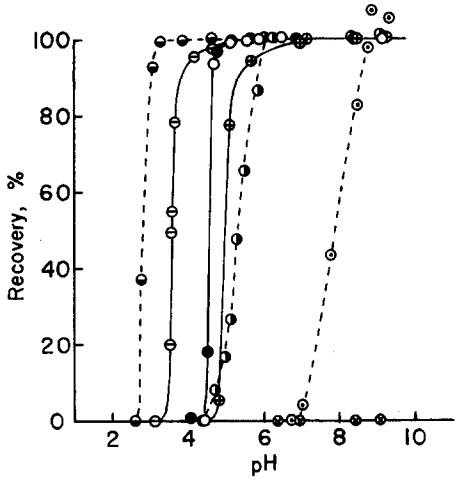

Fig. 2. Effect of pH on the precipitation of oxinates in the presence of CPA. Amount of oxine added 120 mg, —⊖— aluminium 100 μmole (without phosphoric acid), —●— aluminium 100 μmole, orthophosphoric acid 11 mmole, —⊕— aluminium 100 μmole, diluted CPA solution (A) 10 ml, —○— aluminium 100 μmole, --◒-- iron (III) 100 μmole, --◑-- manganese (II) 186 μmole, --⊙-- magnesium 104 μmole, --⊗-- calcium* 122 μmole. The last five systems contained 10 ml of diluted CPA solution (B). The pH value was adjusted by adding ammonia without hydrogen peroxide. Recoveries of elements were calculated on the assumption that the theoretical forms of oxinates to be precipitated were $Al(Ox)_3$, $Fe(Ox)_3$, $Mn(Ox)_2$, $Mg(Ox)_2$ and $Ca(Ox)_2$. * Phosphate was precipitated at pH above 6.3.

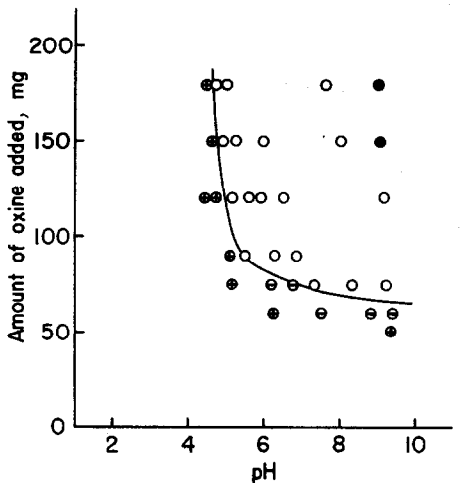

Fig. 3. Effect of pH and amount of oxine added on the precipitation of aluminium in the presence of CPA. Aluminium taken 100 μmole, diluted CPA solution (B) 10 ml, recovery of aluminium ⊕ <98%, ⊖ 98–99%, ○ 99–101%, ● >101%. The solid line roughly shows the boundary of a region where the recovery of aluminium exceeds 99%.

The effect of pH and amount of oxine added was investigated in the presence of diluted CPA solution (B); the results are shown in Fig. 3. Oxine itself may be precipitated from a highly concentrated solution, and the excess of oxine should not be more than 50–100 mg/70 ml.

The precipitation behaviour of the oxinates of iron(III), manganese(II), magnesium(II) and calcium(II) was also examined in the presence of CPA to see whether the method can be applied to samples such as silicate materials. From the results shown by dotted lines in Fig. 2 it is seen that iron and manganese oxinates are precipitated together with aluminium at the recommended pH value of 6.5. Manganese, magnesium and calcium occur in bauxites in only a very small amount, however. Accordingly, the aluminium content can be calculated by subtracting the amount of iron from the sum of aluminium and iron. The precipitation of titanium oxinate is completely suppressed by addition of hydrogen peroxide.

The bromination of oxine is generally performed by adding 1–2 ml excess of the reagent, with Indigo Carmine as indicator.[16,17] However, it is convenient to add 15 ml of 0.11*N* bromine solution without addition of indicator, because bauxites generally contain 50–60% Al_2O_3 and 5–15% Fe_2O_3. The oxidation of iodide by ferric ions is prevented by adding orthophosphoric acid.[16] It is desirable to deoxygenate the

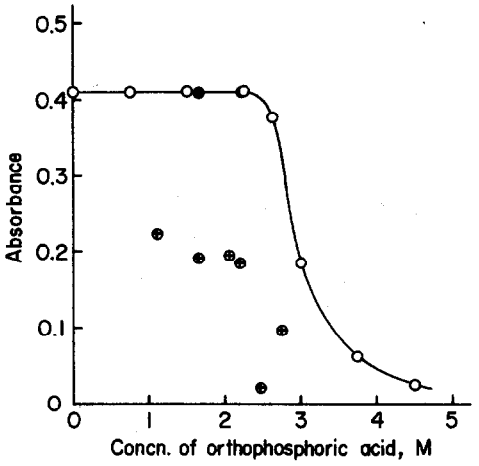

Fig. 4. Effect of orthophosphoric acid and CPA on the solvent extraction of iron with MIBK. Iron(III) taken 102 μg, ○ orthophosphoric acid, ⊕ 300°-CPA* (added immediately after the dilution with water), ● 300°-CPA* [hydrolysed in an analogous manner to the preparation of diluted CPA solution (A) and then added]. The concentration of phosphoric acid was varied at the first stage of extraction. The ensuing manipulation was the same as in the recommended procedure. * The concentration of CPA is expressed in terms of orthophosphoric acid.

sample solution with nitrogen, to minimize interference effects of oxygen.

Photometric determination of iron with 1,10-phenanthroline

The conditions proposed for the extraction of iron[9] were modified as described above because iron in amounts of about 0.1 mg can be extracted quantitatively into MIBK at hydrochloric acid concentrations above 4*M*, and the volume of sample solution taken never exceeded 5 ml.

From the results shown in Fig. 4, it is seen that the extraction of iron is not affected at all by orthophosphoric acid up to a concentration of 2.2*M*, but the recovery is lowered when CPA is added immediately after the dilution with water. The interference from CPA, however, is diminished when the CPA solution is boiled for 15 min to hydrolyse the condensed phosphates.

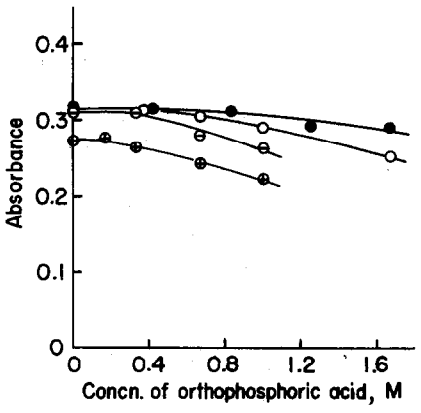

Fig. 5. Effect of concentration of BPHA and orthophosphoric acid on the solvent extraction of titanium. Titanium(IV) taken 20.4 μg, concn. of hydrochloric acid 7.2*M*, concn. of BPHA in benzene ⊕ 0.1%, ⊖ 0.2%, ○ 0.3%, ● 0.5%.

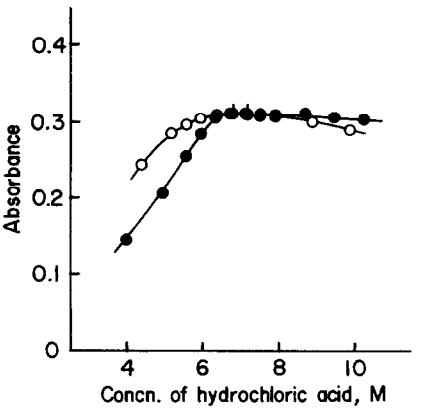

Fig. 6. Effect of the concentration of hydrochloric acid on the solvent extraction of titanium with BPHA. Titanium(IV) taken 20.4 μg, concn. of BPHA in benzene 0.3%, ● without phosphoric acid, ○ 11 mmole of orthophosphoric acid, ◌̇ 10 ml of diluted CPA solution (B).

Photometric determination of titanium with BPHA

Tanaka and Takagi[18] and Ishii and Einaga[19] have proposed sensitive photometric determination methods for titanium with BPHA. Most metal ions do not interfere, but the interference of a large amount of phosphate has not been investigated.

Figure 5 shows the effect of BPHA and orthophosphoric acid concentration. It is seen that the absorbance increases with increasing concentration of BPHA, the magnitude of the effect falling off above 0.2% concentration. The increase in BPHA concentration is also effective in eliminating the interference from orthophosphoric acid. A BPHA concentration of 0.3% was decided on, since few interferences were observed even when the content of CPA in the sample solutions was as high as 1 g.

The effect of the hydrochloric acid concentration was examined at two levels of orthophosphoric acid concentration, *i.e.*, 0 and 11 mmole/30 ml. The results shown in Fig. 6 indicate that the maximum absorbance is obtained in the hydrochloric acid concentration ranges of 6.5–9*M* and 6–8*M*, respectively. It is also clear that interference from 1 g of CPA is not observed at the recommended hydrochloric acid concentration of 7.2*M*.

Determination of aluminium, iron and titanium in bauxites

The content of aluminium was abnormally low in some cases. The results shown in Fig. 7 indicate that a constant value, in close agreement with that obtained by a standard method,[12] is obtained by boiling the reaction mixture for 10 min with hydrochloric acid. Therefore, the low recovery of aluminium may be attributed to the presence of condensed phos-

Table 3. Determination of aluminium, iron and titanium in bauxites

Bauxites	Methods	Sample taken, g	Content, % Al_2O_3	Fe_2O_3	TiO_2
Ranchi (India)	JIS M8361*†	2.0938	54.9	7.26	8.36
		2.0169	54.6	7.24	8.43
	CPA method	0.1034	54.7	7.23	8.35
		0.1012	54.9	7.27	8.48
Weipa (Australia)	JIS M8361	2.0302	59.9	5.17	2.22
		2.0372	60.0	5.17	2.23
	CPA method	0.1020	60.0	5.09	2.24
		0.1022	59.9	5.10	2.24
Sematan (Malaysia)	JIS M8361	2.0080	57.0	7.90	1.89
		2.0094	56.9	7.95	1.87
	CPA method	0.1019	56.7	7.89	1.86
		0.1037	56.7	7.96	1.89
Malay (Malaysia)	JIS M8361	2.0096	53.8	10.34	0.62
		2.0127	53.6	10.33	0.58
	CPA method	0.1060	53.8	10.40	0.56
		0.1017	53.7	10.53	0.57
Ramunia (Malaysia)	JIS M8361	2.0418	55.6	7.15	0.65
		2.0816	55.4	7.16	0.64
	CPA method	0.1029	55.6	7.15	0.62
		0.1012	55.4	7.17	0.63

* Samples decomposed with a mixture of sulphuric acid, nitric acid, hydrochloric acid and water (9:7:2:6 v/v).

† Total of Al_2O_3, Fe_2O_3 and TiO_2 by gravimetry, iron by photometry with EDTA–H_2O_2, titanium by photometry with H_2O_2.

phates. The susceptibility of condensed phosphates to hydrolysis seems to vary from sample to sample, so a longer boiling time of 15 min has been adopted as a recommended condition.

The methods described have been applied to the determination of aluminium, iron and titanium in several kinds of bauxite. The results are shown in Table 3 together with those obtained by the JIS method. It is evident that in general the results for three elements are in acceptably close agreement and of high precision. When 6 samples of Sematan bauxite were analysed as above, the relative standard deviations were 0.1, 0.5 and 0.4% for aluminium, iron and titanium, respectively.

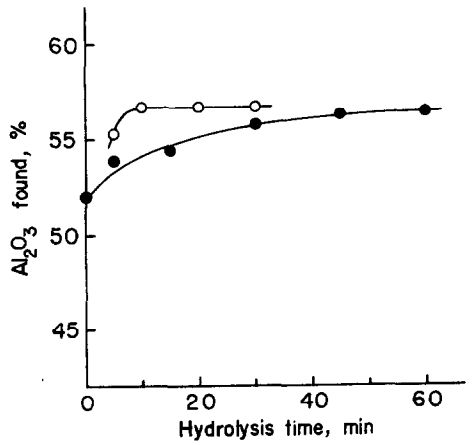

Fig. 7. Effect of the hydrolysis of reaction mixture on the determination of aluminium. Semantan bauxite was decomposed with CPA according to the recommended procedure. The reaction mixture was transferred into a beaker and then boiled for the desired time with (○) or without (●) 1 ml of concentrated hydrochloric acid. The ensuing manipulation was the same as that described under *Procedures*.

The decomposition of bauxites with CPA is rapid, free from tedious and time-consuming manipulations such as digestion of fused products, elimination of silica and filtration, and it is therefore suitable for analysis of large numbers of samples. In the present study, the decomposition of samples was performed at a constant temperature of 300° in specially made quartz tubes. The decomposition, however, can also be done in quartz or platinum crucibles placed on a sand-bath or in a muffle furnace. This decomposition method may also be applicable to the determination of alkali metals and silica in bauxites, for it is accomplished without addition of such metal salts as potassium pyrosulphate, sodium carbonate, lithium metaborate, *etc.*, and this possibility is being studied.

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DETERMINATION OF PLATINUM METALS AND GOLD BY OPTICAL EMISSION SPECTROMETRY WITH A RADIOFREQUENCY INDUCTIVELY-COUPLED ARGON PLASMA SOURCE

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Summary—Optimum operating conditions in a 2-kW inductively-coupled argon plasma source for the detection of the elements platinum, palladium, rhodium, ruthenium, iridium, osmium and gold have been established. Detection limits obtained for aqueous solutions introduced into the plasma by pneumatic nebulization range from 1.5 ppb (Rh) to 34 ppb (Ir). No interelement effects caused by chemical interference have been observed between the elements investigated or from a number of base metals; several spectral interferences were observed with the spectrometer employed. The effect of the presence of mineral acids on the nebulization of sample solutions is reported.

The radiofrequency inductively-coupled plasma (ICP) provides a potentially sensitive and interference-free source for the determination of traces of metallic and non-metallic elements by optical emission spectrometry (OES). With the exception of several isolated reports of detection limits by optical emission spectrometry with the ICP source for some of the elements of the platinum group metals, to the best of our knowledge no systematic studies of the determination of the platinum metals by this technique have been reported. The determination of these elements by ICP–OES is of considerable interest, particularly as their determination by flame atomic-absorption spectrometry (AAS) may be subject to chemical interferences in the condensed phase, so that the use of releasing agents is frequently required.[1–7] This paper reports the results of a study of the determination of Au, Ir, Os, Pd, Pt, Rh and Ru by ICP–OES in a 2.0-kW inductively-coupled plasma source operating at 27 MHz; optimum conditions for the detection of these elements have been established and a study of the interferences between the platinum group metals and the effect of some other elements and mineral acids has been undertaken.

EXPERIMENTAL

Apparatus

The ICP source and spectrometer employed have been described previously;[8] the pneumatic nebulizer used for this work, however, was a glass concentric nebulizer (Meinhard Associates, Model T-230-A2). Argon plasma gas flow was not used, the plasma being supported entirely by the argon coolant and injector gas flow employed.

Reagents

Platinum and gold stock solutions of 1000 μg/ml in 1*M* hydrochloric acid were obtained commercially (BDH Ltd., Poole, Dorset). A commercial 1000-μg/ml stock solution of rhodium in 1*M* hydrochloric acid was also employed (Alfa Products Inc., Beverley, Mass, U.S.A.). Palladium, osmium and iridium stock solutions (1000 μg/ml) were prepared in 1*M* hydrochloric acid from $(NH_4)_2PdCl_4$, $(NH_4)_2OsCl_6$ and Na_3IrCl_6 respectively. The ruthenium stock solution (1000 μg/ml) was prepared in 1*M* hydrochloric acid from $Ru(DMSO)_4Cl_2$ (DMSO = dimethylsulphoxide).

Copper, iron, nickel, sodium and zinc solutions were prepared in 0.1*M* perchloric acid from analytical-reagent grade salts of the metals. All acids used were prepared by dilution of analytical-reagent grade concentrated acids.

Procedure

The emission spectrum between 200 and 450 nm was recorded for each element during nebulization of aqueous standard solutions. The most intense atomic (or ionic) lines of the elements observed in these spectra were examined further. Selection was then made of the line (or lines) of each element showing the highest signal:background ratio and best signal:noise ratios at a compromise viewing height (30 mm) above the work coil and with a forward power of 800 W, for use in further optimization studies. The optimum conditions of forward power, viewing height above the work coil and injector gas flow-rate to provide the lowest detection limits for each element were then determined. For the purposes of this work the detection limit was defined as that concentration of an aqueous solution of the element required to produce an emission signal intensity at the atomic line employed equal to twice the peak-to-peak variation in the background noise. The values given in this paper are the average of five values obtained from separate nebulization of dilute aqueous solutions of each analyte element.

The linearity of the calibration graphs obtained at the atomic lines selected for each element was checked over a wide concentration range.

Interference effects were examined by nebulization of solutions prepared by mixing 5 ml of a 10-ppm solution of each analyte element with 5 ml of an aqueous solution of the interfering ion studied. The atomic line intensity for the analyte element in these mixtures was then compared with that obtained from a solution prepared from 5 ml of 10 ppm analyte solution diluted with 5 ml of distilled water or dilute acid (depending on the interfering ion studied) in order to allow for any variation in nebulizer uptake rate or efficiency which might occur because of

the presence of acid in the stock solution of the interfering ion.

RESULTS AND DISCUSSION

Optimization of plasma operating conditions for the elements studied

The three principal plasma parameters to be investigated in order to optimize conditions for detection of the platinum metals studied were injector gas flow-rate, forward power to the work coil and the height above the work coil at which the analyte emission was monitored. The effect of variation in operating power and viewing height on the detection limits obtained at the preselected lines of the elements was examined for different argon injector gas flow-rates. The results of these experiments are illustrated for gold and platinum in Tables 1 and 2. These results, which are typical of those obtained for each of the elements studied, indicate that the best detection limits are obtained with a high injector gas flow-rate; the plasma background intensity also decreases. All further work was undertaken with an argon injector gas flow-rate of 1.3 l./min. The variation in detection limits with variation in forward power from 600 to 1200 W and viewing heights between 5 and 35 mm above the work coil for iridium, osmium, palladium, rhodium and ruthenium are shown in Table 3. Examination of the data in Tables 1, 2 and 3 shows that in general, as may be predicted from signal-to-background and signal-to-noise considerations, the use of higher power (1000 or 1200 W) leads to degradation in detection limits. Poorer detection limits are also obtained because of high plasma background emission when the analyte emission is viewed near to the core (*i.e.*, low heights of observation) or high in the tail-flame, because of greater noise levels. Table 4 summarizes the optimum operating conditions and detection limits established for the elements studied. The optimum conditions are similar for all of the platinum metals; where little difference in detection limit is observed with variation in forward power the detection limit is quoted at the power which would be the best compromise for simultaneous multielement analysis.

Table 1. Variation in detection limits obtained for gold at 267.59 nm with forward power and height of observation at different argon injector gas flow-rates

Argon injector flow-rate, *l./min*	Height of observation above work coil, *mm*	Detection limits for Au aqueous solutions, *ppm* Forward power, *W* 800	1000	1200
0.5	5	0.10	0.13	0.15
	10	0.05	0.13	0.09
	15	0.015	0.10	0.11
	20	0.012	0.07	0.09
	25	0.013	0.02	0.09
	30	0.013	0.02	0.025
	35	0.03	0.03	0.03
1.0	5	0.05	0.21	0.21
	10	0.014	0.10	0.08
	15	0.009	0.08	0.07
	20	0.01	0.01	0.02
	25	0.01	0.01	0.01
	30	0.02	0.01	0.01
	35	0.02	0.02	0.015
1.3	5	0.10	0.44	0.20
	10	0.04	0.17	0.18
	15	0.014	0.03	0.08
	20	0.01	0.01	0.03
	25	0.01	0.01	0.01
	30	0.015	0.008	0.01
	35	0.02	0.01	0.04

Table 2. Variation in detection limits obtained for platinum at 265.94 nm with forward power and height of observation at different argon injector gas flow-rates

Argon injector flow-rate, *l./min*	Heights of observation above work coil, *mm*	Detection limits for Pt aqueous solutions, *ppm* Forward power, *W* 600	800	1000
0.5	5	0.42	0.45	0.24
	10	0.30	0.25	0.24
	15	0.06	0.18	0.3
	20	0.06	0.34	0.37
	25	0.045	0.14	0.34
	30	0.07	0.08	0.45
	35	0.07	0.08	0.12
1.0	5	0.15	0.54	0.94
	10	0.09	0.45	0.47
	15	0.06	0.13	0.35
	20	0.04	0.07	0.20
	25	0.03	0.03	0.07
	30	0.03	0.04	0.05
	35	0.05	0.04	0.10
1.3	5	0.42	0.69	1.2
	10	0.30	0.66	0.78
	15	0.06	0.14	0.42
	20	0.06	0.06	0.22
	25	0.04	0.04	0.05
	30	0.07	0.03	0.05
	35	0.06	0.04	0.09

Effect of foreign ions and acids on platinum metal determination

In view of reports of mutual interference effects between the platinum metals in their determination by flame AAS, the first interference study undertaken was the examination of such effects in optical emission spectrometry with the ICP system employed here. The effect of the presence of 1000 ppm of each of the other platinum metals on the determination of 10 ppm of analyte platinum metal in aqueous solution was investigated for the seven elements studied. The results obtained are shown in Table 5. With two exceptions no significant mutual interference effects were observed. The effect of 1000 ppm of ruthenium on the signal obtained for 10 ppm of platinum, where a significant enhancement was observed, is attributable to the presence of a weak ruthenium line at

Table 3. Variation in detection limits obtained for iridium, osmium, palladium, rhodium and ruthenium with forward power and height of observation at argon injector gas flow-rate of 1.3 l./min

Element and wavelength, *nm*	Height of observation above work coil, *mm*	Detection limits for aqueous solutions, *ppm* Forward power, *W* 600	800	1000	1200
Iridium,	20	0.08	0.18	0.26	0.34
322.08	25	0.03	0.034	0.18	0.33
	30	0.06	0.035	0.16	0.25
	35	0.08	0.05	0.14	0.25
Osmium,	20	0.05	0.28	0.64	1.1
442.05	25	0.03	0.08	0.10	0.37
	30	0.03	0.014	0.02	0.16
	35	0.03	0.024	0.03	0.035
Palladium,	15	0.04	0.03	0.06	0.07
340.46	20	0.01	0.01	0.03	0.03
	25	0.005	0.005	0.01	0.02
	30	0.004	0.0025	0.004	0.01
	35	0.003	0.002	0.003	0.016
	40	0.004	0.0035	0.004	0.02
Rhodium,	15	0.025	0.022	0.07	0.06
369.24	20	0.0025	0.01	0.03	0.035
	25	0.002	0.0017	0.007	0.013
	30	0.002	0.0014	0.002	0.022
	35	0.002	0.0016	0.0014	0.003
Ruthenium,	15	0.02	0.06	0.025	0.086
372.80	20	0.004	0.02	0.03	0.066
	25	0.0027	0.002	0.005	0.02
	30	0.002	0.002	0.003	0.014
	35	0.002	0.002	0.002	0.003

265.96 nm which interferes at the Pt 265.94 nm line used for Pt determination. No interference of ruthenium with platinum was observed at this concentration when the Pt 299.79 nm line was used for determination of platinum. Osmium suffers a similar interference in the presence of 1000 ppm of ruthenium if the spectral band-pass is broad, owing to the spectral interference from the weak Ru 442.08 nm line at the Os 442.05 nm line employed for its determination; the use of a narrower spectral band-pass may be successfully employed to resolve these lines and overcome this interference.

In earlier work in the determination of the platinum metals with a plasma jet source it was reported that interference was observed from iron, nickel and copper.[9] The effect of these elements on the determination of the platinum metals by ICP optical emission spectrometry was therefore investigated. Solutions (10 ppm) of the seven elements of interest were therefore prepared in the absence and presence of 1000-ppm concentrations of each of the elements copper, iron, nickel and zinc. The emission intensities for these solutions were recorded at the preselected optimum wavelengths for each platinum metal under the established optimum operating conditions. The results obtained are shown in Table 6. With the

Table 4. Optimum operating conditions for detection of the platinum metals by optical emission spectrometry with the ICP source

Element	Wavelength, *nm*	Height of observation, *mm*	Forward power, *W*	Detection limit, *ppb*
Gold	267.59	25	800	10
Iridium	322.08	25	800	34
Osmium	442.05	30	800	14
Palladium	340.46	35	800	2
Platinum	265.94	30	800	30
Rhodium	369.24	30	800	1.5
Ruthenium	372.80	30	800	2

Table 5. Effect of other platinum metals on emission signals obtained for 10-ppm aqueous solutions of analyte platinum metal

Element and wavelength, nm	Effect on signal of presence of 100 ppm of platinum metal							
	—	Pt	Au	Pd	Rh	Ru	Os	Ir
Pt (265.94)	100	—	102	103	104	151	95	98
Au (267.59)	100	105	—	107	100	94	101	97
Pd (340.46)	100	99	100	—	97	103	98	105
Rh (369.23)	100	102	102	102	—	104	103	103
Ru (372.80)	100	100	103	100	98	—	100	105
Os (442.05)	100	97	97	99	97	104	—	101
Ir (322.08)	100	107	103	103	102	104	101	—

exception of the large enhancement observed for osmium in the presence of nickel and copper no effects were observed resulting from chemical or spectral interference from the elements studied. The effect of copper and nickel on the osmium signal at 442.05 nm results from spectral interference and was not observed when the Os 290.90 nm line was employed; the interference may be attributed to second-order diffraction of unassigned lines of Cu and Ni, as it is removed when a glass filter is placed between the source and spectrometer. Table 6 also shows the results obtained in experiments in which the effect of the presence of 1000 ppm of sodium, as sodium chloride, on the signals obtained for 10 ppm solutions of the platinum metals was investigated; no significant ionization or stray-light interference effects were observed.

The sensitivity of the nebulizer–source system to variation in efficiency when dilute mineral acids were introduced was examined by using 10-ppm solutions of the platinum metals and 1, 5 and 10% v/v aqueous solutions of concentrated sulphuric, nitric and hydrochloric acids. As shown in Table 7, the emission intensities obtained were depressed in each case to differing extents as the acid concentration was increased. Somewhat greater depression of the analyte intensities was observed with sulphuric and nitric acids than with hydrochloric acid; these effects are attributable

Table 6. Effect of selected foreign ions on the emission signals obtained for 10-ppm aqueous solutions of platinum metals

Element and wavelength, nm	Effect on signal of presence of 1000 ppm of foreign ion					
	—	Na	Fe(III)	Ni	Cu	Zn
Gold (267.59)	100	98	96	96	99	101
Platinum (265.94)	100	99	102	95	96	100
Palladium (340.46)	100	96	99	95	95	98
Rhodium (369.23)	100	100	98	95	95	97
Ruthenium (372.80)	100	95	93	91	92	97
Osmium (442.05)	100	95	95	$\gg 100$	$\gg 100$	102
Iridium (322.08)	100	99	96	90	91	91

Table 7. Effect of mineral acids on aspiration of platinum metal solutions

Element	Acid	Signal intensities recorded for 10-ppm platinum metal solutions Acid concentration 0	1%	5%	10%
Pt	H_2SO_4	100	92	87	82
	HNO_3	100	92	91	87
	HCl	100	98	93	90
Au	H_2SO_4	100	89.5	84	80
	HNO_3	100	90	86	87
	HCl	100	95	93	93
Pd	H_2SO_4	100	89	85	79
	HNO_3	100	90	90	88
	HCl	100	94	91	90
Rh	H_2SO_4	100	94	88	84
	HNO_3	100	94	91	89
	HCl	100	96	92	91
Ru	H_2SO_4	100	87	83	73
	HNO_3	100	87	85	82
	HCl	100	91	88	87
Ir	H_2SO_4	100	92	83	79
	HNO_3	100	94	90	88
	HCl	100	94	92	91
Os	H_2SO_4	100	96	88	84
	HNO_3	100	97	98	92
	HCl	100	96	99	98

to variation in the uptake rate and efficiency of the nebulizer system with change in the density and viscosity of the solutions aspirated. Although the effects observed are relatively small, the acidity of samples and standards should be matched if high accuracy is to be preserved in analytical procedures. The variation in sensitivity with acid nature and concentration may not, however, be totally due to physical parameters as the effect differs with the elements studied.

CONCLUSION

The present work has shown that the seven noble metals studied can be detected with high sensitivity, freedom from mutual interference effects and interferences from some base metals by optical emission spectrometry with the inductively-coupled argon plasma source. Optimum conditions for the detection of the platinum metals do not vary greatly, so that compromise operating conditions permitting simultaneous multielement analysis are easily established.

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SHORT COMMUNICATIONS

SPECTROPHOTOMETRIC DETERMINATION OF MICRO AMOUNTS OF HYDRAZINE AND HYDROXYLAMINE ALONE AND IN THE PRESENCE OF EACH OTHER

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Summary—Hydrazine and hydroxylamine alone or in the presence of each other are determined at concentrations of 1–10 μg/25 ml with a relative precision of 3–0.8% by using iron(III) in the presence of Ferrozine.

Hydrazine and its derivatives have found application in industry, agriculture and other fields, including the manufacture of metal films, photographic chemicals, explosives, insecticides, and blowing agents for plastics. Hydroxylamine occurs in some biological processes and the reduction of nitrate. Both of these chemicals are used as reducing agents and as reagents for compounds containing carbonyl functional groups. In addition, hydrazine and its analogues are irritants and are suspected to be carcinogens. Thus, their determination at micro levels is of interest.

Microgram amounts of hydroxylamine and hydrazine are individually determined fairly easily by several spectrophotometric methods.[1–7] Mixtures of hydroxylamine and hydrazine have also been analysed chronopotentiometrically by Morris and Lingane,[8] gas chromatographically by Cain and Stevens,[9] and, by measuring acetylation rates, by Malone and Biggers.[10] However, no suitable spectrophotometric methods are described for the analysis of mixtures of small amounts of these compounds. In this note, we present a method for the determination of hydroxylamine and hydrazine individually, as well as in mixtures, at microgram levels, by using the reaction of iron(III) in the presence of the disodium salt of 3-(2-pyridyl)-5,6-bis(4-phenylsulphonic acid)-1,2,4-triazine, "Ferrozine".

EXPERIMENTAL

Reagents

Fresh 0.01*M* solutions of Ferrozine were prepared from the pure reagent. An approximately 0.01*M* solution of iron(III) was prepared either by dissolving 0.56 g of pure iron wire in 10 ml of 6*M* perchloric acid containing 10 drops of nitric acid, or by dissolving ferric ammonium sulphate in dilute sulphuric acid, and diluting to 1 litre. A 0.1*M* iron(III) solution was prepared in the same manner but with some difficulty. A 0.3*M* buffer of pH 3.2 was prepared by adding sodium hydroxide to a monochloroacetic acid solution. Hydroxylamine solution (0.01 *M*) was prepared by dissolving 69.5 mg of hydroxylamine hydrochloride in 100 ml of demineralized water and assayed by the iodometric method.[12] Suitable dilutions were made to obtain 10^{-3} or $10^{-4}M$ solutions of hydroxylamine and hydrazine. Monomethylhydrazine solution, 0.01*M*, was prepared by diluting 0.53 ml of the anhydrous liquid to 1 litre with demineralized water containing a few drops of concentrated sulphuric acid and was analysed by the iodometric method.[12] A 0.01*M* solution of unsymmetric dimethylhydrazine was prepared by diluting 0.76 ml of the anhydrous liquid to 1 litre with demineralized water containing a few drops of concentrated sulphuric acid and standardized by thhe modified Olson bromate–bromine method.[13]

Test solutions for hydrazine and hydroxylamine determinations were prepared by taking suitable aliquots of standard 10^{-3} or $10^{-4}M$ solutions, together with any other species to be investigated.

Procedures

Hydroxylamine alone was determined at room temperature (25°) as follows. A suitable portion of 0.0001*M* hydroxylamine, 3 ml of monochloroacetate buffer of pH 3.2, 1 ml of 0.01*M* Ferrozine and 2 ml of 0.01*M* Fe(III) were added to a standard flask, in that order, and the timing was started immediately after the addition of the Fe(III) solution. The mixture was diluted to the mark, the reaction was allowed to proceed for 7 min and the absorbance was then recorded at 562 nm. Calibration graphs were prepared by plotting absorbance *vs.* concentration of hydroxylamine.

Hydrazine alone was determined by placing a suitable portion of 0.0001*M* hydrazine and 2 ml of 0.01*M* Fe(III) in a beaker and adjusting the pH to 1.8–1.9. The solution was transferred to a 25-ml standard flask, heated at 95° for 25 min, then cooled to room temperature. Next 3 ml of pH-3.2 buffer and 1 ml of Ferrozine were added and the contents diluted to the mark. A few crystals of ammonium hydrogen fluoride were added and the absorbance at 562 nm was measured. A blank determination was carried out in a similar manner but without the hydrazine.

Monomethylhydrazine and 1,1-dimethylhydrazine alone were determined in a manner similar to that used for hydrazine, except that heating was done at 85° for 40 min and 70° for 14 min respectively.

Analysis of mixtures. Mixtures containing hydroxylamine and hydrazine in 1:5 ratio were analysed by using two aliquots. With one aliquot, the absorbance due to hydroxylamine was measured at room temperature after 7 min. In the presence of very large amounts of hydrazine it was desirable to extrapolate the absorbance to zero time from the measurements recorded after 7 min and also to use

Table 1. Determination of hydroxylamine and hydrazines alone

Substance	Temperature, °C	Apparent molar absorptivity, *l. mole.*$^{-1}$ *cm*$^{-1}$	No. of electrons in reduction
Hydroxylamine	30	$3.67 \pm 0.02 \times 10^4$	1.31
Hydrazine	95	$8.51 \pm 0.05 \times 10^4$	3.04
1,1-Dimethylhydrazine	70	$9.93 \pm 0.05 \times 10^4$	3.55
Monomethylhydrazine	80	$9.34 \pm 0.06 \times 10^4$	3.34

larger aliquots. A second aliquot was treated in the same manner as for hydrazine alone; the sample was heated for 25 min at 95°, and the resulting absorbance corresponded to hydrazine plus hydroxylamine. Thus, the amount of hydrazine was found from the difference in absorbance, corrected for the blank: $A_{Hdz} = A_{total} - (A_{Hyd} + A_{blank})$.

When hydroxylamine was in large excess (10:1 ratio to hydrazine, or higher) the hydroxylamine was determined at room temperature as in the previous case. Hydrazine was determined after reaction of the hydroxylamine with iron(III), separation of the unreacted hydrazine by ion-exchange resin, Bio-Rad 50W–X–8, 100–200 mesh, and elution with 0.1*M* sodium chloride and 0.01*M* sodium bicarbonate. The eluate was divided into two portions: one served as a blank and the other was treated in the same manner as for hydrazine alone. The amount of hydrazine could be obtained from the calibration curve obtained by following the same procedure.

RESULTS AND DISCUSSION

The reduction of Fe(III) by hydroxylamine and hydrazine depends on the concentration of Fe(III), pH of the reaction mixture, time of reaction, temperature, and even order of reagent addition. In all determinations, the concentration of iron(III) is kept at 50–100 times that of hydroxylamine and hydrazine, and that of Ferrozine at least 5–6 times that of the iron(III).

Reaction of hydroxylamine, hydrazine, monomethylhydrazine, and 1,1-dimethylhydrazine with iron(III) in the pH range 1.6–1.9 gives reproducible results. The plot of observed absorbance *vs.* concentration gives a straight line with slope corresponding to the apparent molar absorptivity. The number of electrons involved in these reactions is obtained by dividing the apparent molar absorptivity by the molar absorptivity of the iron(II)–Ferrozine complex, 2.8 ± 10^4 l. mole^{-1}.cm^{-1}. The results are summarized in Table 1. Fractional values suggest that iron(III) reactions with hydrazines and hydroxylamines are complex. These reactions have been studied by Higginson and Wright,[14] Rosseinsky,[15] and Cahn and Powell.[16] Hydrazine oxidation by iron(III) apparently follows two major paths yielding varying amounts of NH_4^+:

$$2N_2H_4 + 2e \rightarrow 2NH_4^+ + N_2$$
$$N_2H_4 + 4e \rightarrow N_2 + 4H^+.$$

Similarly, hydroxylamine is oxidized to nitrogen and nitrogen oxides. However, hydroxylamine reacts with iron(III) at room temperature about 2800 times faster than hydrazine does. Thus, the reaction of hydroxylamine with iron(III) at 30° is complete in 3 min, while hydrazine at room temperature reacts only to a very small extent and requires approximately 20 min for complete reaction, even at 95°. Thus, hydroxylamine can be easily determined in the presence of hydrazine at room temperature. Optimum pH for the formation of $[Fe(Ferrozine)_3]^{4-}$ is in the range 3.1–4.0, even though the complex is stable over a wider pH range. Beer's law is followed in the concentration range

Table 2. Analysis of hydroxylamine and hydrazine mixtures

Mixture	Amount, μg/25 *ml* Taken	Found*	Absorbance† A_{T_1}	A_{T_2}	ΔA
Hydroxylamine	5.95	6.00 ± 0.04	0.218	0.786	0.418
Hydrazine	3.85	3.92 ± 0.06			
Hydroxylamine	3.95	3.95 ± 0.05	0.175	0.407	0.232
Hydrazine	2.21	2.20 ± 0.06			
Hydroxylamine	2.65	2.70 ± 0.05	0.120	0.819	0.699
Hydrazine	6.73	6.64 ± 0.06			
Hydroxylamine	3.80	3.89 ± 0.04	0.173	0.590	0.417
Hydrazine	3.83	3.90 ± 0.07			
Hydroxylamine	3.30	3.31 ± 0.05	0.148	0.556	0.408
$(CH_3)_2NH$-NH_2	6.00	6.12 ± 0.07			
Hydroxylamine	6.60	6.72 ± 0.06	0.300	0.920	0.620
$(CH_3)_2N$-NH_2	9.60	9.43 ± 0.08			
Hydroxylamine	2.97	2.90 ± 0.05	0.129	0.672	0.498
CH_3NH-NH_2	5.97	6.10 ± 0.08			
Hydroxylamine	5.12	5.20 ± 0.06	0.233	0.482	0.249
CH_3NH-NH_2	3.22	3.10 ± 0.08			

* Based on five determinations. Hydroxylamine is obtained from the calibration curve, while hydrazines are calculated from the absorbance measurements at temperatures T_1 and T_2.

μg $(NH_2NH_2) = (A_{T_2} - A_{T_1}) \times 9.40$

μg $[(CH_3)_2NNH_2] = (A_{T_1} - A_{T_1}) \times 16.06$

μg $(CH_3NHNH_2) = (A_{T_2} - A_{T_1}) \times 12.31$

† Absorbances, A_{T_1} and A_{T_2}, reported are corrected for the blank corresponding to the temperature used. $T_2 > T_1$.

from 4 to 40 × $10^{-6}M$ for hydroxylamine and from 2 to 20 × $10^{-6}M$ for hydrazine.

In mixtures where the hydrazine concentration is much greater than that of hydroxylamine, the absorbance change due to the hydrazine reaction becomes measurable even at room temperature, hence absorbance readings are taken for an additional 6 min or so beyond 7 min and are extrapolated to zero time to yield the value for hydroxylamine. The results for mixtures containing different amounts of hydroxylamine and hydrazine are presented in Table 2. The relative precision for the determination of hydroxylamine changes from 3 to 1% with increasing concentration, while that for hydrazine varies from 5 to 2%.

When the amount of hydrazine is very small, compared to the amount of hydroxylamine, a preliminary reaction with iron(III) at room temperature coupled with ion-exchange separation provides a method for determination of hydrazine. However, the method is tedious and should be used only when time is of no consequence.

All substances which are capable of reducing iron(III), such as iodide, ascorbic acid, cysteine, semicarbazide, *etc.*, and also substances (anions) such as fluoride, cyanide, which are able to complex iron(III), must be absent. Cobalt(II) yields a positive error, while manganese(II) and copper(II) yield a negative error. Nitrite (NO_2^-) has no appreciable effect in the determination of hydroxylamine at room temperature. If iron(II) is present in the samples, it can be determined by direct reaction with Ferrozine, and a correction applied to the determination proper.

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SYNERGIC EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) AS TERNARY COMPLEXES WITH *N*-HYDROXY-*N*-*N'*-DIARYLBENZAMIDINES AND ANISALDEHYDE

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Summary—*N*-Hydroxy-*N*,*N'*-diarylbenzamidines react with vanadium(V) in anisaldehyde medium to form 1:2:1 (metal:hydroxyamidine:anisaldehyde) greenish-blue complexes over a wide pH range in chloroform solution. On the basis of the strong synergistic effect in formation of these ternary complexes an extraction–photometric method for microgram amounts of vanadium(V) has been developed and applied to standard steel samples.

N-Hydroxy-*N*,*N'*-diarylbenzamidine, a monobasic and bidentate chelating agent, reacts with vanadium(V) in the presence of acidic substances, including carboxylic acids phenols *etc.*, to form 1:1 adducts in chloroform solution.[1] It also reacts with vanadium(V) in the presence of various aromatic aldehydes, *e.g.* benzaldehyde, cinnamaldehyde, anisaldehyde, to form 1:1 greenish-blue adducts. This method may be compared with the established PBHA method.[2–5] According to Shendrikar,[6] Ti(IV), Zr, Mo(VI), W(VI), Ag^+ and Tl^{3+} interfere seriously in the determination of V(V), and Mn^{2+} and Cr^{3+} are also found to interfere. Some authors[7,8] have shown that the extraction is not quantitative because of partial reduction of V(V) in relatively concentrated hydrochloric acid solution. Most of these disadvantages have been overcome in the present method. The extraction is quantitative and Ti(IV), Zr, Mo(VI), Ag^+, Tl^{3+}, Mn^{2+} and Cr^{3+} do not interfere. The method provides a new and convenient solvent-extraction and photometric determination of vanadium(V) with various *N*-hydroxy-*N*,*N'*-diarylbenzamidines in the presence of anisaldehyde.

EXPERIMENTAL

Reagents

A stock solution of vanadium(V) was prepared by dissolving ammonium metavanadate in doubly distilled water and standardized volumetrically by the permanganate method.[9]

Hydroxyamidines were prepared by condensation of equimolar quantities of *N*-aryl-*p*-toluimidoyl chloride and the corresponding *N*-arylhydroxylamine in ether medium.[10,11] The resulting hydrochloride was treated with dilute ammonia to liberate the free base which was crystallized from benzene–petroleum ether (2:1). All the compounds gave satisfactory C,H and N analysis.

Procedure

Transfer an aliquot of vanadium(V) solution containing 100 μg of metal to a separatory funnel, dilute to 25 ml with distilled water and adjust the pH 2.0 with 2*M* hydrochloric acid or ammonium acetate. Add 10 ml of 0.06*M* reagent solution and 5 ml of 0.03*M* anisaldehyde solution (both in chloroform) and shake for 2 min. Separate the chloroform layer and dry over anhydrous sodium sulphate. Wash the aqueous phase with two 4-ml portions of chloroform. Transfer the extracts to a 25-ml standard flask and make up to volume with chloroform. Measure the absorbance at λ_{max} against chloroform as a blank.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of vanadium(V)-hydroxyamidine complexes in the absence and presence of anisaldehyde are shown in Fig. 1. The vanadium–hydroxyamidine complexes show a flat peak between 580 and 590 nm with molar absorptivity of about 1.7×10^3 l.mole^{-1}.cm^{-1}. The absorbance of these complexes is unstable and gradually increases with time. In the presence of anisaldehyde a stable 1:1 greenish-blue adduct is formed with λ_{max} in the region 610–615 nm, with molar absorptivity of about $5.0–5.7 \times 10^3$ l.mole^{-1}.cm^{-1}. A strong synergistic effect

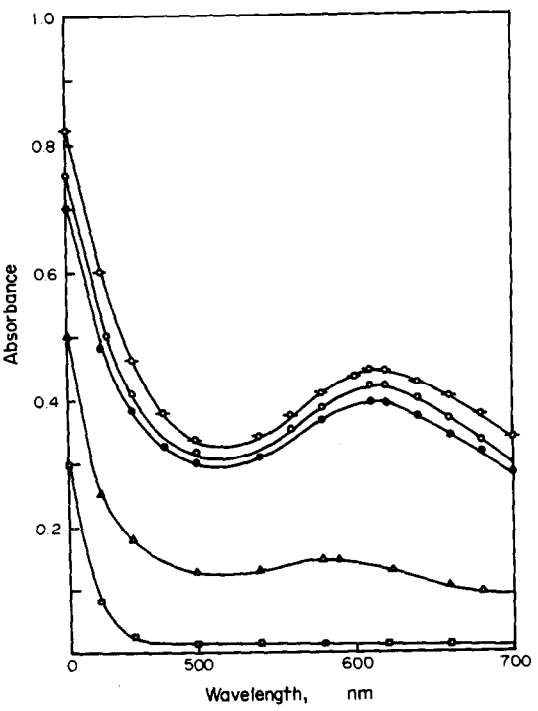

Fig. 1. Absorption spectra. -○-7.85 × 10^{-5}*M* V + 0.002*M* HCPCMPTA + 0.02*M* anisaldehyde ○-7.85 × 10^{-5}*M* V + 0.002*M* HPCMPTA + 0.02*M* anisaldehyde ●-7.85 × 10^{-5}*M* V + 0.002*M* HTCMPTA + 0.02*M* anisaldehyde Δ-7.85 × 10^{-5}*M* V + 0.002*M* HCPCMPTA □-0.002*M* HCPCMPTA

Table 1. Spectral data for vanadium–hydroxyamidine–anisaldehyde complexes in chloroform

Characteristics	*N*-hydroxy-*N*-*p*-chlorophenyl *N*-(3-chloro-4-methylphenyl)-*p*-toluamidine	N-hydroxy-*N*-phenyl-*N'*-(3-chloro-4-methyl-phenyl)-*p*-toluamidine	*N*-hydroxy-*N*-*p*-tolyl-*N'*-(3-chloro-4-methylphenyl)-*p*-toluamidine
Optimum pH range	0.5–3.5	1.0–4.5	0.8–4.0
Optimum vanadium conc. range for Beer's law, *ppm*	0.6–8.4	1.0–8.6	1.2–9.0
Optimum vanadium conc. range (Ringbom plot), *ppm*	1.0–7.4	1.2–8.0	1.6–8.0
λ_{max}, *nm*	615	610	610
ϵ, *l. mole*$^{-1}$*.cm*$^{-1}$	5.7×10^3	5.3×10^3	5.0×10^3
Relative std. devn. %*	0.5	0.7	0.7

* Twelve measurements for 4 ppm of vanadium.

is observed, as shown by the hyper- and bathochromic shift on adduct formation.

Effect of variables

Of the various solvents tried, chloroform was found to be best as the reagents were highly soluble in it and the complexes were readily extracted. The pH was adjusted with 2*M* hydrochloric acid and ammonium acetate. The optimum pH ranges are listed in Table 1. Generally a four-fold molar excess of hydroxyamidine and at least a 200-fold excess of anisaldehyde are required for complete extraction of the vanadium(V). Variation in temperature from 20° to 35° does not affect the absorbance values. The extracts are stable for at least 30 hr at 27 ± 2°.

Nature of complexes

The ratio of vanadium(V) to hydroxyamidine in the ternary complexes was determined by the mole-ratio[12] and continuous-variation methods.[13] The ratio of vanadium to anisaldehyde was determined by a curve-fitting method[14] (plot of log absorbance *vs.* log [anisaldehyde]). The results obtained show the formation of a 1:2:1 (metal:hydroxyamidine:RCHO) complex.

Effect of foreign ions

The tolerance limits for foreign ions (in ppm) in the determination of 4 ppm of vanadium(V) with an error less than 2% are given in parentheses: chloride, bromide, iodide, nitrate, sulphate, triethanolamine, urea, thiourea, borate, selenate, acetate, phthalate and alkali metals (1200); alkaline-earth metals (800); lanthanides (1000); Cu^{2+} (200); Cd^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Al^{3+}, Cr^{3+} and Ag^{+} (500); Mn^{2+} (400); Mn(VII) (300), UO_2^{2+} (500); citrate and tartrate (600); Tl^{3+} (800); Nb(V) and Ta(V) (100), Ti(IV) (40); Zr(IV) (60); Mo(VI) (200); phosphate (800), arsenate (400). The interference due to iron(III) is eliminated by masking with trisodium phosphate. Tungstate interferes seriously.

Table 2. Determination of vanadium in BCS* steels

Steel	Found,† %	Certified value, %	Std. devn.
64a Alloy	1.56	1.57	0.007
241/1 High-speed	1.55	1.57	0.008
252 Low alloy	0.45	0.46	0.004

* British Chemical Standards, Bureau of Analysed Samples, Ltd., Newham Hall, Middlesbrough, Yorks.

† Mean of 6 results.

Determination of vanadium in steel samples

The validity of method was tested with two vanadium–tungsten steels and a tungsten-free steel. The results obtained with *N*-hydroxy-*N*-*p*-chlorophenyl-*N'*-(3-chloro-4-methylphenyl)-*p*-toluamidine are shown in Table 2. The sample, containing about 3 mg of vanadium, was dissolved in nitric acid (2 + 3). Tungsten, if present, was removed as the hydrated oxide before the determination of vanadium.

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TIN(II) SULPHATE AS A NEW REDUCTIMETRIC TITRANT—DIRECT TITRATION OF THALLIUM(III) WITH USE OF ION-PAIR AND REDOX INDICATORS

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Summary—The use of tin(II) sulphate as a direct reductimetric titrant for thallium(III) has been investigated, with potentiometric and visual detection of the end-point. Some azure dyes are used as redox indicators and Methylene Blue is used as both a redox and an ion-pair indicator.

Several indirect but few direct reductimetric methods are known for thallium(III). Some of the titrants used for direct reduction are titanium(III),[1] hydrazine sulphate,[2] thiosulphate,[3] ascorbic acid,[4,5] vanadium(II),[6] chromium(II)[7] and hydroquinone.[8] Wetton and Higginson[9] have studied the reaction between thallium(III) and tin(II) and observed that the reaction is quite rapid in about 1.3*M* hydrochloric acid medium. Basińska and Tylżanowska[10,11] have reported potentiometric and visual end-point detection in the direct estimation of thallium(III) with tin(II) chloride in hydrochloric acid medium. The potentiometric method gave results up to about 1% lower than those obtained by the iodometric method and this was attributed to occlusion of $TlCl_3$ in the TlCl precipitate formed.

Tin(II) sulphate is known to be more stable than tin(II) chloride.[12] Qualitative experiments have shown the formal redox potentials of Sn(IV)/Sn(II) in sulphuric acid medium to be similar to those in hydrochloric acid medium. The difficulty involved in their exact determination has been reported by Bock and Greiner.[13] The formal redox potential of the Tl(III)/Tl(I) system is higher in sulphuric acid than in hydrochloric acid medium.[14] Therefore tin(II) sulphate in sulphuric acid medium should be a better reductant with larger potential breaks at the equivalence point for the estimation of thallium(III). We have now established suitable conditions for this titration.

EXPERIMENTAL

Reagents

Thallium(III) hydroxide was prepared as reported earlier[15] and dissolved in sulphuric acid. The solution was standardized by the iodometric method.[16]

Stannous sulphate was prepared according to Carson[17] and used at an overall acidity of 1–2*M* sulphuric acid since lower acidity is not suitable.[18] The solution was standardized by the method of Donaldson and Moser[19] and stored under carbon dioxide.

Aqueous solutions (0.1%) of Methylene Blue, Thionine, Toluidine Blue O, Azure A, Azure C and New Methylene Blue were used.

Pontentiometric titrations

Measure the potential with a platinum wire indicator electrode and a standard calomel electrode: use a sodium sulphate agar bridge. Keep the titration solution in an atmosphere of carbon dioxide.

Titrations with visual end-point detection

Methylene Blue as ion-pair indicator. In a 150-ml titration cell take 80 ml of 1*M* sulphuric acid, 5 ml of ~0.05*M* thallium(III) (in 1*M* sulphuric acid) to which enough hydrochloric acid is added for its concentration to be about 0.1*M* at the end-point, and 2 drops of Methylene Blue solution. Fit the titration cell with a 3-holed rubber stopper accommodating the burette tip and inlet and outlet tubes for carbon dioxide. Pass carbon dioxide through the solution for about 5 min, then titrate with stannous sulphate. The end-point is shown by the sharp colour change from violet pink to blue.

Methylene Blue as redox indicator. Place 50 ml of concentrated hydrochloric acid and 30 ml of boiled-out distilled water (cooled) in the 150-ml titration cell described above. Add 5 ml of ~ 0.05*M* thallium(III) in sulphuric acid and 2 drops of Methylene Blue solution. Pass carbon dioxide through the solution for about 5 min and titrate with tin(II) sulphate, very slowly near the end-point, which is shown by the disappearance of the blue colour.

RESULTS AND DISCUSSION

Stability of tin(II) sulphate in 1M sulphuric acid

About 150 ml of tin(II) sulphate in 1*M* sulphuric acid were left in the open in a 400-ml beaker; 10-ml portions were analysed for tin(II) content by the method of Donaldson and Moser.[19] The tin(II) was fairly rapidly oxidized, the concentration being 0.0496*M* initially, 0.0454*M* after 4 hr and 0.0328*M* after 20 hr. After 48 hr the solution was turbid. When a similar solution was kept in an atmosphere of carbon dioxide, the concentration decreased by 0.8% in 7 days.

From the results in Table 1, however, it is clear that negative errors are observed when there is precipitation of thallium(I) chloride. It is known that increase of chloride concentration increases the solubility of thallium(I) chloride.[20,21] Thus in solution containing higher concentrations of chloride precipitation of thallium(I) chloride is prevented, and it also does not occur at low chloride concentration if the thallium concentration is not too high ($pK_{sp} = 3.7$). Hence the low results reported by Basińska and Tylżanowska[10] can be avoided if the chloride concentration is above or below a certain range, and the thallium concentration is kept below a certain limit.

Potentiometric titrations

It was found that the potential break at the end-point decreased if the sulphuric acid concentration was increased, being 560, 520, 490, 470 and 440 mV/0.05 ml for 1, 2, 3, 4 and 6*M* sulphuric acid. An acid concentration below 1*M* is not suitable because the tin(II) sulphate is hydrolysed.[18] The optimum medium is 1–2*M* sulphuric acid. Air should be removed from the solutions as tin(II) is susceptible to oxidation by air. The maximum error

Table 1. Pontentiometric titration of thallium(III) sulphate (0.343 mmole) with tin(II) sulphate

Experiment	Conditions	Remarks	Volume of tin(II) sulphate: Theoretical, *ml*	Volume of tin(II) sulphate: Experimental, *ml*	Error, %
1	1*M* H_2SO_4 + Cl^-(1.4 mmole)	No precipitate	6.70	6.70	0.0
2	1*M* HCl	Precipitate (TlCl)	6.70	6.64	−0.9
3	3*M* HCl	do.	6.70	6.63	−1.0
4	5*M* HCl	No precipitate	6.70	6.68	−0.3
5	6*M* HCl	do.	6.70	6.71	+0.2
6	8*M* HCl	do.	6.70	6.69	−0.2

found for titration of 0.14–0.72 mmole of thallium(III) was 0.2%.

Iron(III), mercury(II), copper(II) and nitrate interfere in the potentiometric titration.

Visual end-point detection

Thallium(III) is known to form a violet-pink product with Methylene Blue[22] in the presence of chloride, whereas thallium(I) does not. Thallium(III) does not give the pink product in the absence of chloride. Therefore the effect of the chloride:thallium ratio and hydrochloric acid:sulphuric acid ratio on the titration, with Methylene Blue as indicator, was investigated. The results are summarized in Table 2.

Experiments 1–7 suggest that Methylene Blue does not function as an indicator unless the concentration of chloride is at least four times that of the thallium, in agreement with the known formation of a violet-pink ion-pair between $TlCl_4^-$ and positively charged Methylene Blue.[22] Experiments 8–11 show that the indicator functions in the same way for sulphuric acid concentrations up to 3*M*. At higher concentrations of the acid the indicator ceases to function.

Experiments 12–19 show that with 1*M* hydrochloric acid, though the colour change is from violet pink to blue, there is a considerable error because of precipitation of TlCl and strong adsorption of thallium(III) on it. With increase in hydrochloric acid concentration the error becomes positive and the indicator action unsatisfactory, but with 6–8*M* hydrochloric acid the results are satisfac-

Table 2. Effect of variation of the concentration of Cl^-, HCl and H_2SO_4, on the titration of thallium(III) with tin(II) sulphate, with Methylene Blue as ion-pair and redox indicator

Experiment No.	Tl(III) : Cl^- ratio or [HCl]	[H_2SO_4] *M*	Volume of $SnSO_4$ used, *ml*: Theoretical	Volume of $SnSO_4$ used, *ml*: Experimental	Colour change at the end point	Remarks	Error, %
1	2:1	1.0	4.23	—	—	No pink product formed	—
2	1:1	1.0	4.23	—	—	do.	—
3	1:2	1.0	4.23	—	—	do.	—
4	1:4	1.0	4.23	4.22	Violet pink to blue	The pink colour changes to blue when all the Tl(III) is reduced to Tl(I)	−0.2
5	1:6	1.0	4.23	4.22	do.	do.	−0.2
6	1:10	1.0	4.23	4.22	do.	do.	−0.2
7	0.1–0.2*M*	1.0	4.23	4.22	do.	do.	−0.2
8	0.1–0.2*M*	2.0	4.03	4.02	do.	do.	−0.2
9	0.1–0.2*M*	3.0	4.03	4.02	do.	do.	−0.2
10	0.1–0.2*M*	4.0	4.03	—	—	No pink product is formed	—
11	0.1–0.2*M*	5.0	4.03	—	—	do.	—
12	1.0*M*	1.0	4.23	4.00	Violet pink to blue	In the solution the pink colour disappears but persists on the TlCl precipitate formed, owing to adsorption.	−5.0
13	2.0*M*	1.0	5.25	5.38	Blue to colourless	Pink product is formed locally and disappears during stirring; solution becomes turbid during titration, owing to TlCl formation.	+2.7
14	3.0*M*	1.0	5.25	5.38	do.	No pink product. Solution becomes turbid during titration, owing to TlCl.	+2.7
15	4.0*M*	1.0	5.25	5.31	do.	No pink product. Dye is reduced to colourless leuco form. No turbidity.	+1.2
16	5.0*M*	1.0	5.25	5.31	do.	do.	+1.2
17	6.0*M*	1.0	5.25	5.26	do.	do.	+0.2
18	7.0*M*	1.0	5.25	5.26	do.	do.	+0.2
19	8.0*M*	1.0	5.25	5.26	do.	do.	+0.2

tory, but the colour change at the end-point is now from blue to colourless because the Methylene Blue under these conditions is reduced to the leuco form by tin(II).

Similar experiments with thionine, New Methylene Blue, Azure C, Azure A and Toluidine Blue 0 showed that these dyes also function as redox indicators in this titration, with a change from blue to colourless, but they do not function as ion-pair indicators. They are therefore used only in media that are 6–8*M* in hydrochloric acid. The results obtained for 0.1–1.1 mmole of thallium(III), by use of these indicators, were satisfactory, the maximum error being 0.4%.

Interferences. Perchlorate interferes when Methylene Blue is used as an ion-pair indicator. Hg^{2+}, Hg_2^{2+}, Fe^{3+} also interfere, but oxalate, acetate, Zn^{2+} and Cd^{2+} do not.

Conclusions

The advantage of the method is that the hydrochloric acid concentration can range up to 8*M*. This is useful in the estimation of thallium in complexes with strong organic ligands, which can easily be brought into solution by addition of a large amount of hydrochloric acid. A further advantage over use of tin(II) chloride is that tin(II) sulphate is more stable and very large potential breaks are obtained for titrations in sulphuric acid medium.

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ABSORPTION OF NITROGEN DIOXIDE IN ORGANIC SOLVENTS

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Summary—The absorption of NO_2 at low levels in nitrogen, by *N,N*-dimethylformamide (DMF) and dimethyl sulphoxide (DMSO), has been investigated. Parts-per-million levels of NO_2 were collected with an efficiency of 90% in DMF and 65–70% in DMSO. The absorption efficiency in DMF depends on the gas flow-rate and the bubbling time, but in DMSO it is independent of time.

Nitrogen dioxide is often scrubbed from air streams or preconcentrated for its quantitative determination in aqueous solution: aqueous alkali, aqueous sulphuric acid, and chelating agent solutions have been used.[1–4] The Jacobs–Hochheiser procedure for the measurement of atmospheric levels of NO_2 involves the use of a gas bubbler filled with dilute sodium hydroxide. As half of the nitrogen dioxide passing through this solution is thought to be converted into nitrite, the U.S. Environmental Protection Agency has adopted a factor of 0.35, taking into consideration also the absorption efficiency. The factor for this method when aqueous solutions are used has occasionally aroused controversy.[5] The use of an organic solvent as the absorption solution would avoid this uncertainty.

There are only a few reports in the literature of values for the solubilities of oxides of nitrogen in non-aqueous solvents. Garber and Wilson[6] indicated that NO_2 was absorbed in dimethyl sulphoxide (DMSO), and Arvia and co-workers[7,8] reported that NO_2 produced by oxidation of nitrite was dissolved quantitatively in DMSO and in acetonitrile.

The purpose of this study was to measure the efficiency of collection of NO_2 in some organic solvents and to evaluate the possibility of determining atmospheric NO_2 after collection in an organic solvent.

EXPERIMENTAL

Reagents and apparatus

All organic solvents, of guaranteed reagent grade, were dried and then distilled. All other chemicals used were of guaranteed reagent grade.

Standard gas supply equipment (Stec Co., SGGU-14) was used to obtain ppm-levels of NO_2 in nitrogen. Absorbances were measured with a spectrophotometer (Hirama Rika Co., SP-6B). Nitric oxide was determined with a chemiluminescence NO_x analyser (Shimadzu Seisakusho Co., Model CLM-401). Kinoshita gas absorbing bottles (G-2 fritted bubbler, 50 ml) were used as absorption vessels.

Procedure

A known concentration of NO_2 in nitrogen was passed through a needle valve and a rotameter to a fritted bubbler which contained 50 ml of the organic solvent. Another bubbler, containing 10 ml of Saltzman's absorption solution, was placed in series and the amount of NO_2 carried over and trapped in this solution was determined. The gas flow-rate was dependent on the suction provided by a pump. The two bubblers were located in a water-bath, controlled at 25 ± 0.1°. The amounts of NO_2 in the standards and carried over in the absorption experiments were all determined by Saltzman's method,[9] because many organic solvents containing nitrogen affect the NO_2 value as measured by the chemiluminescent method.

RESULTS AND DISCUSSION

Preliminary experiments indicated that *N,N*-dimethylformamide (DMF) and dimethylsulphoxide (DMSO) were satisfactory solvents for NO_2 while pyridine, acetonitrile and hexamethylphosphoramide were poor solvents.

The absorption efficiencies of NO_2 in DMF and DMSO were measured for gas bubbling times appropriate for the concentrations and the method (Table 1) and the reproducibility was good. The effects of gas flow-rate and gas bubbling time on the absorption efficiency were studied for ppm levels of NO_2 (Fig. 1). The efficiency remained constant over the range 2–7 ppm. Lower concentrations were difficult to prepare reproducibly. We may conclude that DMF is a reasonably good absorption medium for NO_2: the efficiency found in these experiments is comparable with that for Saltzman's absorption solution, which was found to be 91% at 300 ml/min flow-rate. The gas flow-rate does affect the solubility, but the effect is smaller for DMF

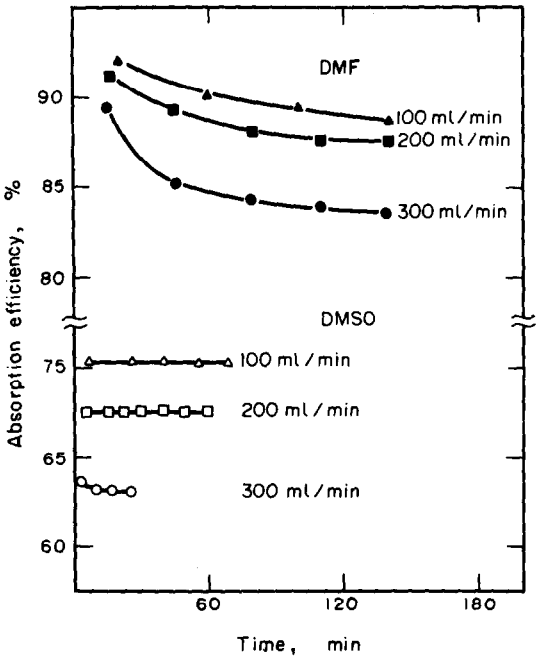

Fig. 1. Absorption efficiency as a function of bubbling time.

Table 1. Absorption efficiency of NO_2

Solvent	Flow rate, *ml/min*	Bubbling time *min*	NO_2 concentration, *ppm*	Absorption efficiency, %
DMF	100	40	2.65	91.7
		45	2.95	94.1
		45	2.95	94.2
	200	30	2.99	92.8
		30	2.99	92.6
		30	3.42	91.2
	300	30	2.38	89.1
		30	3.43	89.5
		30	3.43	89.7
DMSO	100	12	2.97	70.4
		12	2.97	70.6
		15	4.20	70.5
	200	6	5.72	67.1
		7	3.23	67.7
		7	3.23	67.8
	300	5	3.90	64.5
		5	3.90	64.6
		5	6.99	66.1

than for DMSO. The collecting efficiency is independent of time with DMSO, but decreases with time in the initial stages of absorption in DMF. Because of the low recovery in DMSO, the Saltzman solution in the second bubbler was rapidly saturated and prolonged absorption measurements could not be carried out.

Nitric oxide was examined by the same procedure and found not to be absorbed in DMF or DMSO. The water contents of the solvents, which were less than 0.1%, had no influence on the efficiency.

From the results, DMF and DMSO, especially DMF, are found to be good absorption media for NO_2. If the absorbed NO_2, which remains unchanged in the solvent, is determined directly in the DMF, a higher sensitivity is possible than when aqueous absorption solutions are used. An electrochemical determination of the NO_2 collected in organic solvents is under investigation.

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FEASIBILITY OF HIGH-FREQUENCY FIELD-MODULATION FOR ZEEMAN-MODULATED ATOMIC-ABSORPTION SPECTROMETERS

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Summary—Some advantages of alternating field modulation for Zeeman background-correction are discussed. A technique for applying such modulation to a conventional hollow-cathode lamp is examined. The technique is used to provide a very simple conversion of a Techtron AA3 spectrometer to Zeeman background-corrected operation.

Existing designs of Zeeman-modulated (ZM) spectrometers show a number of technical disadvantages. These include the large and massive magnets usually needed to generate the required field strengths, the sensitivity losses observed for lines which split to give an anomolous multiplet, and the need for (usually expensive) ultraviolet-transmitting polarizers, often in combination with a birefringent modulator, which are required to separate the π and σ components of a transverse multiplet. In addition, unwanted noise may reduce ZM spectrometer sensitivity: source- and atomizer-modulated instruments are subject to self-absorption noise and to schlieren noise respectively, for reasons discussed elsewhere.[1]

All these problems may be overcome if the various multiplet components are distinguished by a.c. field modulation, such as has been demonstrated by Uchida and Hattori,[2] rather than by the currently favoured polarization methods. Alternating current field modulation is not very practicable with iron-cored magnets, however, since the resulting inductance of the magnet winding becomes sufficiently high to preclude modulation frequencies greater than a few Hz. Elimination of the core removes this limitation, and high-frequency a.c. field modulation then becomes viable. The price to be paid for elimination of the magnet core is a correspondingly increased current in the field coils. Hence ohmic power dissipation is also correspondingly increased, and heat removal by some means other than natural heat conduction through the windings becomes essential.

EXPERIMENTAL

In the present experiments a longitudinal field was generated at the cathode of a conventional hollow-cathode lamp, positioned at the centre of an annular field coil. The field strengths generated by the coil were measured by insertion of a 1 cm diameter search coil at the position normally occupied by the lamp cathode, while the field coil was driven at the 50 Hz mains frequency. Measurement of the a.c. voltage developed across the search coil permitted the field coil to be calibrated in terms of its drive current.

Field coil design

The field coil consisted of 600 turns of 22-gauge magnet wire, broken after 300 turns to permit the two 300-turn sections to be driven in series, in parallel, or from independent power supplies. The resistances of the two sections of the coil were 3.5 and 4.0 Ω; during use they carried a maximum peak current of about 60 A. The coil was wound on a tubular glass former of 4 cm internal diameter, which will just accept a hollow-cathode lamp of the type supplied, for example, by Varian–Techtron. The coil was wound over a 4 cm length of the former to a depth of 4 cm (Fig. 1), then tissue paper was glued to the outer layer of the coil with contact adhesive, and coated with epoxy resin to form a water jacket. The weight of the completed coil was under 500 g; its size and weight are therefore sufficiently small to permit its ready incorporation into certain types of commercially available atomic-absorption spectrometers.

The longitudinal field configuration given by this arrangement is convenient for two reasons. First, the electric and magnetic axes in the neighbourhood of the lamp cathode are almost coincident, and magnetic stability of a d.c. cathode plasma is therefore automatically conferred.[3] The data of Fig. 2 illustrate this point: cathode emission remains almost unaffected by the longitudinal field (although the anode plasma was observed to become quite distorted). The second advantage is that the π components of a longitudinal Zeeman multiplet are not observed. Thus if square-wave field modulation is used, atomic-absorption measurements are made at zero field, while the background correction is obtained on the σ components of the multiplet without recourse to polarizing optics. This is an ideal configuration since atomic absorption of the σ components

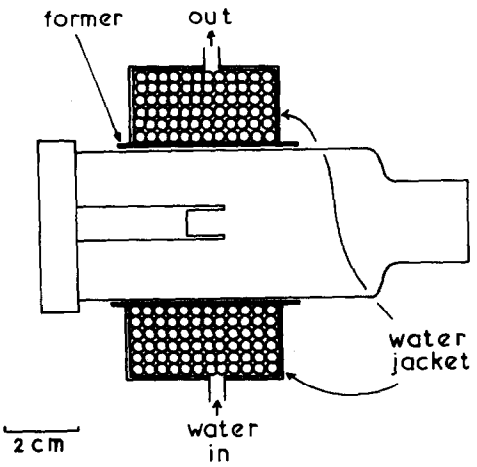

Fig. 1. Field coil and lamp. The plane containing the circular coil winding lies perpendicular to the plane of the paper.

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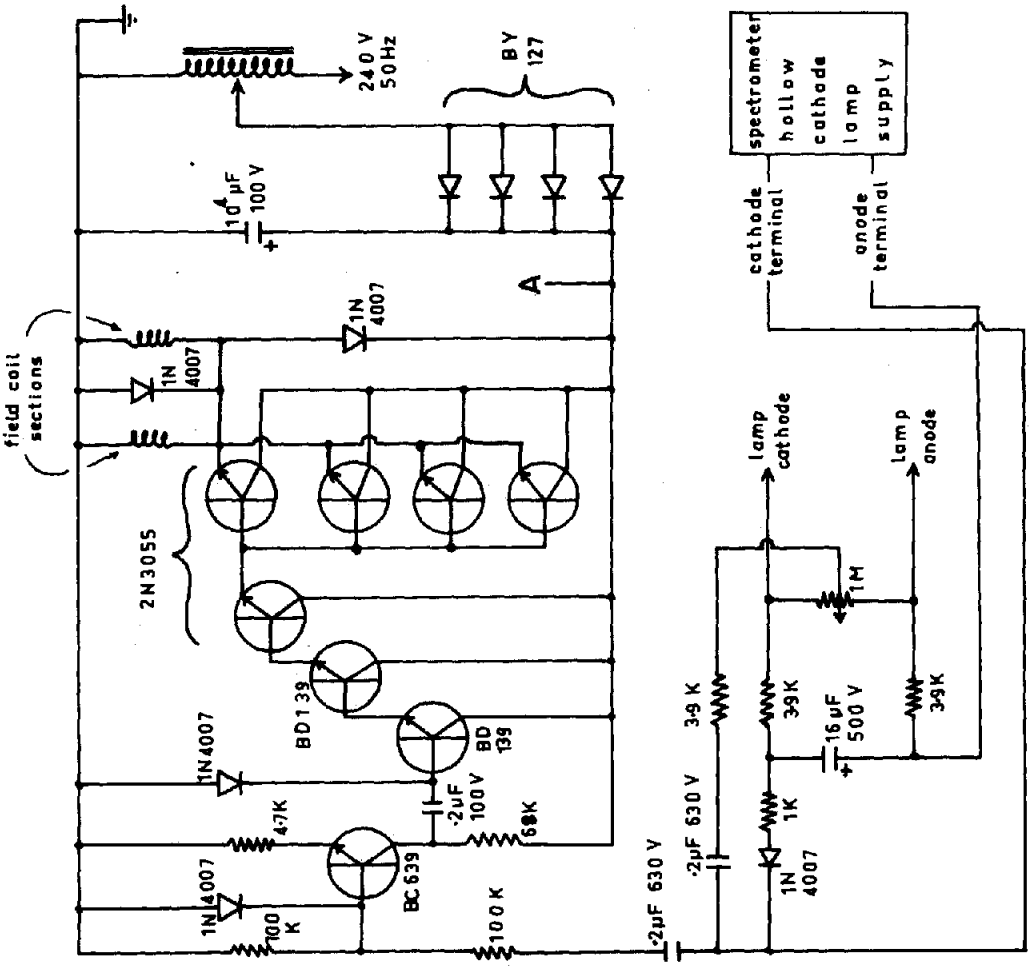

Fig. 3. Field-coil driving circuit. The d.c. conversion for the lamp supply and the amplifier front end were designed specifically for the AA3. Some modification may be necessary for other spectrometers. No phase control of the drive signal was provided since the AA3 does not use lock-in amplification.

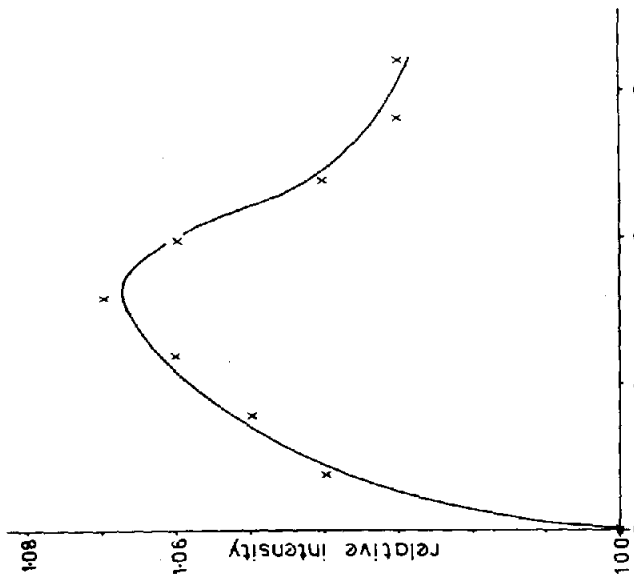

Fig. 2. Intensity of the Cu 3248 Å line vs. longitudinal field strength. Data were collected on the AA3 with the lamp driven directly from the spectrometer power supply, and were normalized with respect to the zero-field signal.

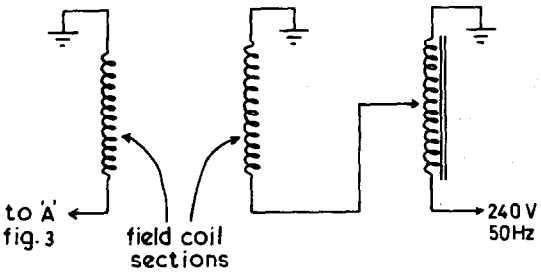

Fig. 4. 3.5 kW field-coil drive.

can always be reduced (to zero if required) simply by increasing the magnetic field strength, without affecting the magnitude of the zero-field absorption signal, a situation which cannot be achieved by polarization selection of the π and σ components of a transverse multiplet unless these take the form of a normal Zeeman triplet.

Experimental operation of the field coil

The technique was tested in practice on a Techtron AA3 spectrometer, using an air–acetylene flame atomizer. The instrument was modified only by addition of the field coil and its power supply. The field coil was mounted at the end of the optical rail and the lamp inserted so as to occupy the customary position for conventional operation. The lamp power-supply output of the spectrometer was connected to the circuit shown in Fig. 3. The high-voltage section of this circuit converts the lamp supply output into a d.c. voltage, upon which a modulation of variable phase and amplitude can be superimposed (for reasons discussed later). This essentially d.c. voltage was used to drive the lamp: since the drive was d.c., only a noise signal was observed on the spectrometer when the lamp was turned on.

The spectrometer lamp supply also modulated the drive circuits for the field coil (Fig. 3). The two coil segments were run in parallel for this purpose, to enable the power-supply output voltage to be kept below about 70 V. The ZM atomic-absorption signal therefore appeared at the usual frequency (50 Hz) to which the main amplifier was tuned. The current pulses to the coil were observed to follow a 50-Hz square wave, showing the inherently high-frequency response expected for the arrangement. The power supply shown in Fig. 3 was designed to use available components. These limited the maximum power which could be delivered to the coil to about 1 kW. At this maximum power dissipation the peak field generated was about 1.5 kG.

The maximum power which the present coil could dissipate was established by connecting the two sections of the coil separately, one directly to the d.c. supply powering the drive circuit in Fig. 3, and the other to a second variable autotransformer (Fig. 4). In this way a sinusoidal 50-Hz field could be obtained by simultaneously increasing the d.c. and a.c. voltages, and the resulting ZM signal again appeared at the response frequency of the spectrometer amplifier. Under these conditions, the maximum combined power dissipation of the two coils was found to be about 3.5 kW, at which a peak field of 4 kG was generated. At this power dissipation the epoxy skin of the water jacket reached a temperature of about 50° after 1 min of operation with a cooling water flow-rate of 2 l./min.

RESULTS

Spectroscopic response

To test the spectroscopic response of the system, ZM signals were measured for the Cu 3248 Å line. This line was selected since the results of Grassam *et al.*[4] have shown that measurable ZM signals can be expected at fields as low as 1 kG. It was found initially that the slight plasma perturbation indicated in Fig. 2 caused a small, unwanted amplitude-modulation of source intensity by the alternating magnetic field. This was offset by applying current modulation to the lamp to generate a cancelling phase-inverted signal (see above).

ZM detection limits for Cu with use of the coil-driving circuits of Figs. 3 and 4 were found to be 0.5 ppm in both cases at the minimum response time of the instrument. No attempt was made to improve this figure, since the AA3 is inherently unsuitable for high-sensitivity work under the present conditions (mainly owing to its use of a tuned rather than a phase-sensitive amplifier; for the same reason, optimization of magnetic field strength is rather critical with this particular instrument in order for a well-defined ZM signal to be observed).

Conclusions

It is felt that the present experiments have demonstrated both the feasibility of utilizing non-cored coils for the field generation in ZM spectrometers, and also the associated technical advantages thereby obtained. The coil size used for this work is considered to be a minimum, since increased power dissipation would be inconvenient (owing to the necessarily increased capacity of all electrical components, together with the simultaneously increased difficulty of avoiding local hot spots on the winding), while power dissipation could not be reduced below the range used here without severely reducing the signal magnitudes observed. Useful improvements in the field strength developed could be obtained by increasing the coil size, to permit a greater number of turns of a heavier gauge of wire to be used.

Acknowledgement—The author is indebted to the Chemistry Department of the University of Newcastle for support of this work.

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SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM AFTER EXTRACTION AS VANADIUM(III) PICOLINATE

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Summary—Vanadium(V) is conveniently reduced by sodium dithionite to vanadium(III) which is extracted as its picolinate complex into chloroform. Vanadium is determined spectrophotometrically by measuring the absorbance of the complex at 385 nm against a reagent blank, Beer's law being obeyed over the range 1–50 μg/ml. The method is one of the most selective, being free from interference by relatively high concentrations of almost all the important elements, titanium, chromium, manganese, iron, cobalt, nickel, zinc, copper, aluminium, molybdenum, tungsten and uranium, found in industrial alloys. Only bismuth interferes. The method is quite simple and rapid. It has been successfully applied for the analysis of vanadium in a variety of samples.

In natural and industrial products, vanadium has to be determined at various concentrations in presence of one or more of the transition elements chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper and occasionally titanium, niobium, platinum, palladium and zinc.[1] Also, uranium and aluminium may be present. Not more than a few milligrams of some of these elements are tolerated even in the best of the existing methods. Iron interferes in a majority of them and is encountered in almost all samples.

Reagents with suitably located nitrogen and oxygen donor atoms have been found to be important chelating agents for vanadium determination. Introduction of various substituents into hydroxylamine, hydroxamic acid, and phenolic and other reagents has served only to improve the sensitivity and not the selectivity of their reaction with vanadium. Picolinic acid is found to give an extractable yellow complex with vanadium(III) in slightly acidic solution. Qualitative tests show that most of the transition elements do not form extractable coloured complexes under the conditions of vanadium extraction. Therefore, picolinic acid has been studied for the extractive spectrophotometric determination of vanadium.

EXPERIMENTAL

Reagents

A vanadium stock solution (10 mg/ml) was prepared from sodium metavanadate, standardized by titration with iron(II),[2] and diluted to 100 and 10 μg/ml. Standard stock solutions of other elements (1–10 mg/ml) were prepared by dissolving suitable salts in water, dilute sulphuric or dilute hydrochloric acid.

Chloroform. The fraction distilling at 60° was used.

Picolinic acid. An 8% solution in water, neutralized with sodium hydroxide.

Decomposition of samples

Rutile. Open up the finely powdered sample (1.0 g) by fusing[3] with 5 g of fusion mixture in a platinum crucible for nearly 30 min. After cooling, dissolve the melt in hot water. Filter off the insoluble residue on a Whatman No. 41 paper and wash 4 or 5 times with 5 ml of hot water each time. Acidify the filtrate to litmus with dilute sulphuric acid and boil to expel carbon dioxide. Filter off any precipitate formed and wash with two 5-ml portions of hot water. Cool the filtrate and washings and make up to 50 ml in a standard flask. Use a suitable aliquot for determination of vanadium.

High speed steel. As described earlier.[4]

Procedure

Transfer a nearly neutral sample solution containing 0.025–1.25 mg of vanadium to a 150-ml separatory funnel. Add 4 ml of picolinic acid reagent and dilute to 20 ml with distilled water. Add 0.7–2.0 g of sodium dithionite, stopper the funnel and shake the contents gently for 1 min. Extract the aqueous phase with two 10-ml portions and one 5-ml portion of chloroform, shaking each time for 1 min, filtering each extract through a small dry Whatman No. 41 paper into a 25-ml standard flask, using the second and third extracts to wash the paper, and make up to the mark with chloroform. Measure the absorbance of the yellow solution at 385 nm in 1-cm silica cells against a similarly treated reagent blank. The absorbance remains constant for at least 1 hr.

RESULTS AND DISCUSSION

Vanadium(V) is reduced to vanadium(III) by shaking a nearly neutral solution for about a minute with sodium dithionite.[4] Vanadium(III) forms a yellow complex with picolinic acid which can be extracted with chloroform. The absorption spectrum is shown in Fig. 1. The complex absorbs very strongly at wavelengths shorter than 300 nm and so does the reagent blank. The absorbance of the latter, however, decreases rapidly to a constant low value at wavelengths longer than 310 nm but the complex shows an absorption maximum at 385 nm, which is chosen for measurements.

The effect of various factors on the extraction is shown in Table 1. In these studies, 20 ml of aqueous phase containing 24 ppm of vanadium were extracted with 20 ml of chloroform and the absorbance was measured at 385 nm after a single extraction. The effect of picolinic acid concentration was studied by using 1.0 g of sodium dithionite and 1 min of equilibration. Adjustment of pH was not required as addition of sodium dithionite (0.7–2.0 g) to a nearly neutral solution was sufficient to give the optimum pH value for maximum extraction. On the basis of these studies, the optimum conditions for maximum absorbance are: 4–6 ml of neutralized 8% picolinic acid solution, pH 4–4.5, 0.7–2.0 g of sodium dithionite, 1–5 min of equilibration with chloroform. Use of the lower end of these ranges gave the extraction results shown in Table 2. Use of chloroform gives the highest absorbance. All the other solvents tried, except dichloromethane, show much lower extraction of the complex. Carbon tetrachloride, methyl

Table 1. Effect of various parameters on the extraction of V(III) picolinate

Picolinic acid solution, *ml*			0.5	1.0	2.0	4.0–6.0	8.0
Absorbance			0.208	0.355	0.561	0.660	0.651
pH	1.1	1.5	2.0	2.6	3.6	4.0–4.5	5.1
Absorbance*	0.429	0.507	0.562	0.597	0.621	0.640	0.615
Dithionite, *g*	0.1		0.5		0.7–2.0		
Absorbance	0.160		0.648		0.660		
Equilibration time, *min*	0.5		1–5				
Absorbance	0.649		0.660				

* Slightly lower than maximum due to oxidation of vanadium(III) during pH adjustment.

Table 2. Extraction of vanadium(III) picolinate by various solvents

Solvent	Absorbance
Chloroform	0.660
Dichloromethane	0.641
Nitromethane	0.312
Isoamyl alcohol	0.116
n-Butyl alcohol	0.096
Benzene	0.027

Table 3. Effect of anions on vanadium(III) picolinate extraction

Salt added*	Amount, *g*	Absorbance†
None	—	0.660
Sodium chloride	3	0.683
Sodium sulphate	2	0.683
Sodium acetate	0.5	0.660
Sodium tartrate	0.07	0.660
Potassium citrate	0.02	0.660
Thiourea	0.5	0.610
Potassium oxalate	0.10	0.414
Sulphosalicylic acid	0.50	0.405
EDTA	0.10	0.000
Potassium hydrogen fluoride	0.10	0.000

* First four added before, rest after reduction.
† After a single extraction with equal volume of solvent.

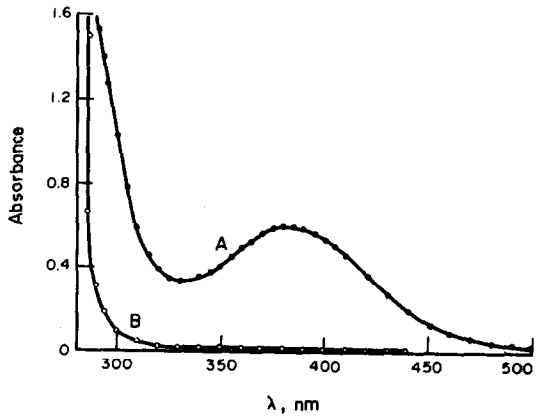

Fig. 1. Absorption spectrum of V(III) picolinate in chloroform. A—V, 24 μg/ml, measured against reagent blank; B—reagent blank measured against chloroform.

isobutyl ketone, isoamyl acetate, n-hexane, cyclohexane and 1,2-dichloroethane do not extract the complex at all. Three extractions with (10 + 10 + 5) ml of chloroform remove 99.8% of the vanadium from 20 ml of aqueous phase, a single extraction with an equal volume giving 90% removal.

The colour is stable for at least an hour and obeys Beer's law over the vanadium concentration range 1–50 μg/ml. Vanadium(III) is known[5,6] to form a 1:3 complex with picolinic acid. The composition of the complex extracted into chloroform is probably the same.

Effect of diverse ions

The effect of various anions in the aqueous phase is shown in Table 3. The presence of chloride and sulphate

Table 4. Behaviour of other ions under the proposed conditions

Ion*	Concentration *mg/20 ml*	Absorbance†
Sr(II), Ba(II)	100	0.006
Cr(III,VI)	100	0.005
As(V)	100	0.005
Ca(II)	100	0.003
Nb(V)	5§	0.002
Re(VII)	1	0.002
Cd(II), U(VI)	50	0.002
Pd(II)	10	0.001
Fe(II,III), W(VI), Zn(II), Al(III)	100	0.000
Cu(II), Mn(II), Pb(II), Be(II), Mg(II), Ce(IV)	100	0.000
Mo(VI), Ni(II), Co(II)	50	0.000
Pt(IV)	20	0.000
Ti(IV), Zr(IV), Th(IV), Sn(II), Sb(V)	20§	0.000

* Initial oxidation state in brackets.
† No visible colour.
§ Sodium tartrate (70 mg) added to prevent hydrolysis.

Table 5. Analysis of samples by the proposed method

Sample composition Matrix*	V added, μg	V found, μg
Fe(10) Ce(20) Ni(13)	400	400, 399
Al(30) Zn(10) Cr(10)	250	250
Mo(20) W(15) Mn(60) Zn(10)	550	550, 548
W(50)	400	400
Al(100)	660	660, 659
U(15) Fe(10) Cr(12) Ti(5)	850	848, 849
Ni(6) Pt(2) Pd(2)†	1000	1000, 1002
Al(40) Zn(7) Cu(2.5) Fe(0.35)§	100	100, 99
Fe(5) Ni(2.3) Cr(2) Mn(0.1)‡	100	100
Rutile (V = 0.125%)#	—	0.122%
High-speed steel, super rapid extra 500	0.87[a]	0.85%

* The number in brackets indicates mg of element in the aliquot taken for analysis.
† Analogous to Palau.
‡ Analogous to Nichroloy (cast).
§ Analogous to V-alloy.
# By ferron method.[4]
[a] Reported value.

slightly increases the extraction of the complex, probably by salting-out. Acetate (0.5 g) has no effect on the extraction, higher amounts decrease the absorbance. Complexing ions decrease the absorbance very much. Tartrate (70 mg) and citrate (20 mg) can be tolerated. Thiourea and oxalate lower the extraction considerably. EDTA and fluoride even in small amounts mask the vanadium completely. In presence of phosphate, the colour fades continuously even after extraction.

In the reduction with dithionite the elements behave in the way already reported.[4] However, the residual amounts of copper, aluminium, zinc, uranium, titanium, antimony and tin picolinates are not extracted. The hydrolysable ions of titanium, thorium, zirconium, tin, antimony and niobium cause emulsions, but addition of 70 mg of sodium tartrate (upper limit of its tolerance), before the dithionite reduction, prevents hydrolysis of the amounts shown in Table 4.

The extraction behaviour of different elements under conditions of the procedure is shown in Table 4. The tolerance limits can be seen from the contribution to the absorbance when the ions are present alone. Tungsten, iron, nickel, cobalt, chromium, molybdenum, zinc and aluminium decrease the extraction of vanadium, probably by consuming reagent to form non-extractable complexes. This effect can be overcome by adding 2–3 times as much picolinic acid as prescribed in the procedure and, in the case of tungsten, also sodium tartrate to the just alkaline sample solution. Under these conditions, the tolerance limits (mg) for these elements in 20 ml of solution are tungsten (50), iron (10), nickel (20), cobalt (50), chromium (20), molybdenum (50), zinc (10) and aluminium (100).

Applications

The proposed method is very selective for vanadium determination in the presence of large amounts of iron, chromium, nickel, cobalt, copper, manganese, molybdenum, tungsten, titanium, zinc, aluminium, uranium, which are important interfering elements in many existing methods. Once the sample is prepared, the determination takes less than 10 min. It is sufficiently sensitive and should be useful in the analysis of many vanadium-containing alloys and other industrial products.

The wide applicability and scope of the method is shown by the satisfactory analysis of a variety of samples (Table 5), without separation of the elements associated with vanadium. Vanadium can be estimated in molybdenum, aluminium, chromium and tungsten compounds.

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A COLORIMETRIC METHOD FOR THE DETERMINATION OF NITRAZEPAM

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Summary—A simple colorimetric method for the determination of nitrazepam is described. Nitrazepam dissolved in ethyl alcohol (95%) produces a yellow anion on addition of aqueous sodium hydroxide, and this is measured spectrophotometrically. The method has been applied to pharmaceutical formulations containing nitrazepam.

The object of this investigation was to develop a simple colorimetric method for the estimation of nitrazepam in pharmaceutical formulations. The B.P. method[1] involves non-aqueous titration with perchloric acid. Colorimetric,[2–4] gas chromatographic,[5–7] differential pulse polarographic,[8,9] and fluorimetric[10] methods have been reported.

This paper presents a new colorimetric method for determining nitrazepam, based on measurement of the absorbance of the deprotonated form. The method has been successfully applied to determination of the drug in pharmaceutical dosage forms containing nitrazepam and certain other drugs in combination.

EXPERIMENTAL

Reagents

Nitrazepam, checked for purity by the B.P. 1973 method,[1] and used as a 0.100% solution in ethanol (95%). Sodium hydroxide solution, 0.5%. Ethyl alcohol (95%), spectroscopic grade.

Procedures

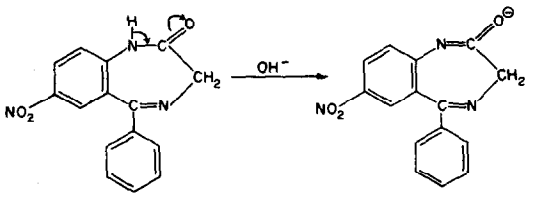
Calibration curve. Prepare a series of solutions of the drug with concentrations ranging from 20 to 100 μg/ml in ethanol (95%) by diluting 1, 2, 3, 4 and 5-ml portions of the 0.100% standard solution to 50 ml with ethanol (95%). Accurately measure out 1 ml (in duplicate) from each prepared solution into a series of 10-ml standard flasks. To each, add 1 ml of 0.5% sodium hydroxide solution and after 10 min dilute to volume with distilled water. Measure the absorbances at 366 nm (λ_{max}) against a blank solution prepared with 1 ml of ethanol instead of drug solution.

Drug assay. Weigh 50 mg of sample, dissolve it in ethanol (95%) and make up to volume with ethanol in a 50-ml standard flask. Analyse a 3-ml portion of this solution by the procedure used for the calibration curve, with 1-ml aliquots.

Assay of tablets. Weigh 20 tablets and grind them to powder in a glass mortar. Accurately weigh a portion of the powder equivalent to about 3 mg of the drug and extract it with 25 ml of warm ethanol (45 ± 2°). Filter with a porosity-4 sintered-glass filter, washing the residue with three 5-ml portions of warm ethanol. Cool the filtrate and washings to room temperature and make up to volume in a 50-ml standard flask with ethanol. Complete the determination as before with 1-ml aliquots.

RESULTS AND DISCUSSION

In the presence of a strong base such as sodium hydroxide, nitrazepam undergoes deprotonation[11] to give a yellow anion which has maximum absorbance at 366 nm (Fig. 1).



The absorbance is not affected by the temperature of reaction. The intensity of the colour produced becomes maximal and constant with 1 ml or more of 0.5% sodium hydroxide under the conditions stated in the procedure. The time required for the complete analysis is about 30 min. Recovery experiments with the bulk drug gave a mean recovery of 100.1%, standard deviation 0.6%.

Effect of other pharmaceuticals

Promazine, chloropromazine hydrochloride, sodium phenobarbitone *etc.* were tested for interference in the method as they are likely to be given in combination with nitrazepam. Since no market products of this type were available, mixtures prepared in the laboratory were used. The results are shown in Table 1.

Recovery studies

Known amounts of nitrazepam were added to the previously analysed formulations and these mixtures were analysed by the proposed method. These results are also tabulated in Table 1.

The results obtained show that the procedure gives a convenient method for assay of nitrazepam, alone or in

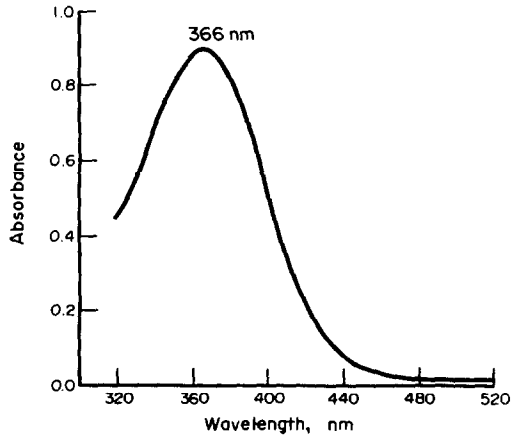


Fig. 1. Absorption spectrum of nitrazepam in alkaline medium.

Table 1. Recovery studies on 5-mg portions of nitrazepam

Additive (5 mg)	Nitrazepam recovery, %	Recovery of added nitrazepam (5 mg), %
—	100.2	100.3
—	99.9	101.0
Chlorpromazine hydrochloride	100.1	99.5
Promazine	100.0	100.1
Sodium phenobarbitone	100.3	100.3
Meprobamate	100.1	100.1
Chlorodiazepoxide	99.6	99.8
Analgin	99.7	99.9
Paracetamol	101.2	100.2
Diazepam	100.7	100.0
Phenacetin + Analgin	99.9	99.9
Phenylbutazone	101.0	99.8
Chlorapheneramine maleate	99.0	100.0
Cyclizine hydrochloride	99.8	101.0
Dimenhydrinate	99.9	100.0

The first two samples were CIPLA formulations (B.P. assay 98.0 and 98.6% recovery). Results are means of duplicates.

presence of certain drugs and of excipients normally present in commercial dosage forms. The method will not work in the presence of other species giving rise to absorption at the wavelength used.

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SPECTROPHOTOMETRIC AND SPECTROFLUORIMETRIC INVESTIGATION OF AGGREGATION OF SOME ANTHRAQUINONE DERIVATIVES

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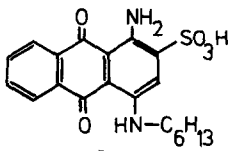
Summary—The behaviour of some anthraquinone derivatives in aqueous solution has been studied by absorption and fluorescence spectrophotometry. The results point to the presence of molecular aggregates in solution, also confirmed by polarographic determinations

The aggregation of anthraquinone dyes in aqueous solution has been the object of numerous studies. Among the investigational methods used we may mention polarography,[1,2] spectrophotometry[3] and diffusion coefficient measurements.[4] The presence of aggregates with a mean degree of association ranging from 2 to 5 has been reported.

The present note reports on the results of experimental studies on the aggregation of some anthraquinone derivatives, performed by spectrophotometric, spectrofluorimetric and polarographic methods.

EXPERIMENTAL

The compounds investigated, **I–III**, were synthesized and purified by the methods described in the literature.



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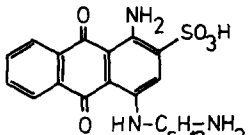
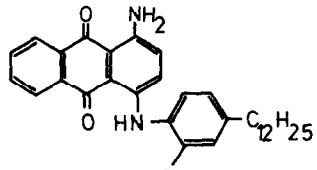


I

Their purity was tested spectrofluorimetrically as well as by elemental analysis. Absorption determinations were carried out with a Shimadzu QV 50 spectrophotometer. Spectrofluorimetric measurements were performed in the same apparatus with a GF-16E accessory for fluorimetry, both 90° and reflection geometry being used. All determinations were performed at room temperature.



II

Polarographic measurements were made with an OH-104 or 105 instrument (Hungary) by the square-wave technique.[1,2]

RESULTS AND DISCUSSION

As seen from Figs. 1–3 the absorption spectra of compounds **I–III** show a concentration dependence in aqueous solution in the 10^{-4}–$10^{-1}M$ range. This is shown by a general hypsochromic and a slight bathochromic effect observed as the concentration is increased, a phenomenon that can be ascribed to molecular aggregation.

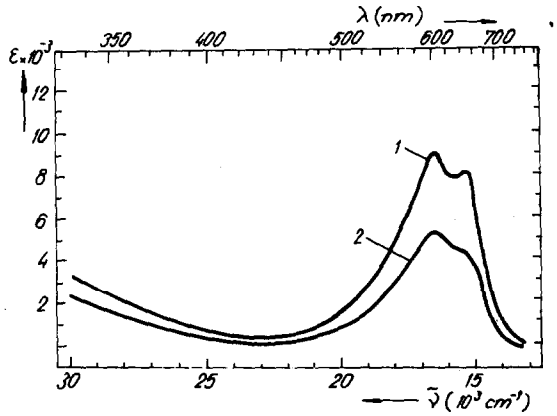


Fig. 1. Absorption spectra of compound I in water at the concentrations $5 \times 10^{-4}M$ (curve 1) and $10^{-2}M$ (curve 2).

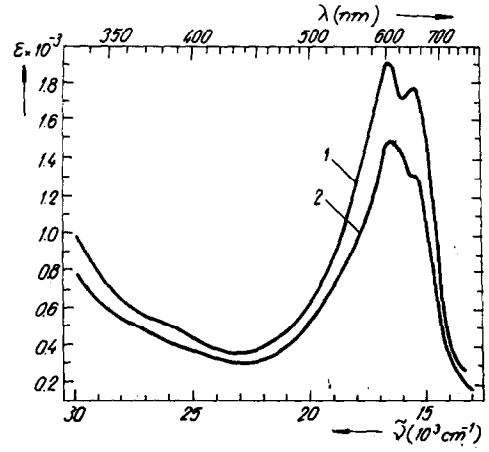


Fig. 2. Absorption spectra of compound II in water at the concentrations $5 \times 10^{-4}M$ (curve 1) and $10^{-2}M$ (curve 2).

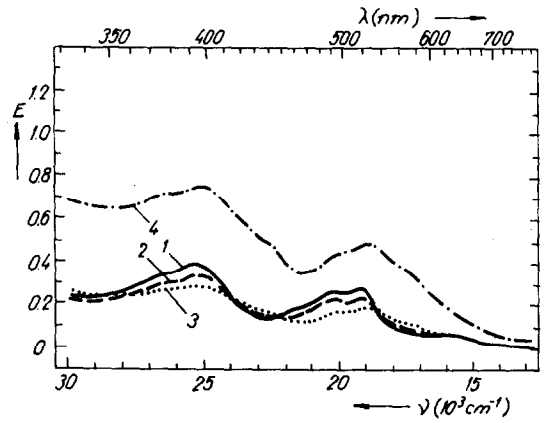


Fig. 3. Absorption spectra of compound **III** in water at the concentrations $10^{-4}M$, 1-cm cell (curve 1); $10^{-3}M$, 0.1-cm cell (curve 2); $10^{-2}M$, 0.01-cm cell (curve 3); $3 \times 10^{-2}M$, 0.01-cm cell (curve 4).

To elucidate the behaviour of compound **III** (the only fluorescent compound) fluorimetric measurements were performed with 90° geometry (Fig. 4). Such measurements were possible owing to the rather strong fluorescence emission of this compound at 555 nm. In the 10^{-6}–$10^{-4}M$ concentration range there was a linear dependence between the logarithm of the fluorescence intensity (log I_r) and the logarithm of the concentration (log c), with a constant fluorescence efficiency. This proves that no molecular interactions involving the fluorochromic centre occur within this concentration range. The inner filter effect prevented us from performing determinations at higher concentrations with the same geometry. To avoid this effect, fluorescence measurements at higher concentrations were performed with reflection geometry. Excitation measurements at three wavelengths (285, 400 and 475 nm) point to a non-linear dependence of log I_r on log c; the curve has a maximum. This suggests the presence of molecular aggregates in the system.

The measurements at the three wavelengths stated were processed by plotting log I_r (as a percentage of the maximum value) against log ϵc and shifting the curves along the ordinate until the linear ascending regions were superimposed, I_r then becoming independent of excitation radiation intensity. It can be observed that I_r is dependent on concentration: it starts to decrease at $7 \times 10^{-4}M$ (Fig. 5) for all three curves. This is evidence for the fluorescence decrease being due to internal molecular interactions.

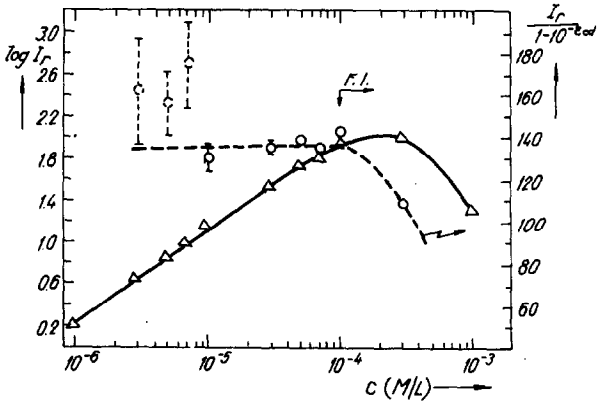


Fig. 4. The dependence of the logarithm of the relative fluorescence intensity and of the $I_r/(1-10^{-\epsilon cd})$ ratio on log c, for compound **III** in aqueous solution; $\lambda_{ex} = 400$ nm, $\lambda_{em} = 560$ nm. Geometry 90°; layer thickness 1-cm; FI—inner filter effect.

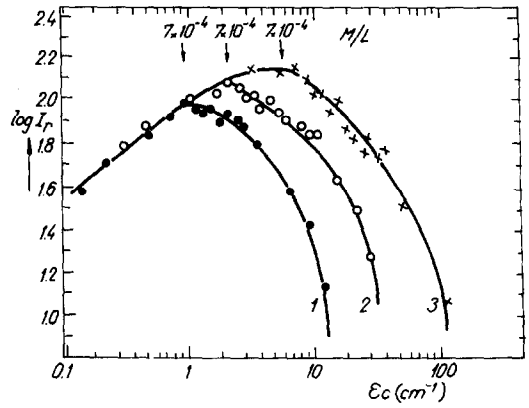


Fig. 5. The dependence of the logarithm of the relative fluorescence intensity of compound **III** in aqueous solution, $\lambda_{em} = 560$ nm, on log (ϵc) for $\lambda_{ex} = 475$ nm (● ●), $\lambda_{ex} = 400$ nm (after translation, ○ ○), and $\lambda_{ex} = 285$ nm (after translation, × ×). Reflection geometry.

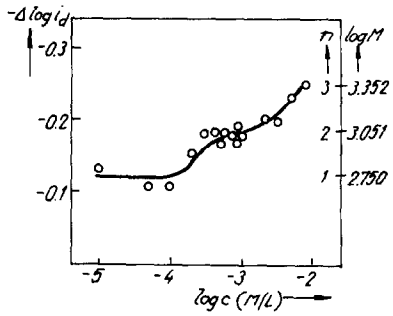


Fig. 6. The dependence of the logarithm of the difference between the limiting diffusion current for compound **III** in buffer solution (0.025M aminoacetic acid and 0.075M NaCl, at pH 3) and that for the Cd^{2+} ion (—Δlog i_d), and the dependence of the mean degree of aggregation (n), and molecular weight (log M) on the logarithm of the concentration (log c).

The appearance of molecular aggregation was detected by Hillson and McKay's polarographic method.[2] As seen from Fig. 6, aggregation starts at $10^{-4}M$ in presence of the electrolyte contained in the buffer and increases considerably for concentrations up to $5 \times 10^{-3}M$. It was not possible to determine the mean degree of aggregation for this concentration range, as the curve showed sharp increases.

The conclusion is that all three dyestuffs undergo molecular aggregation at concentrations above about $10^{-4}M$.

Acknowledgement—Thanks are due to Dr. I. Voicu, Institute for Atomic Physics, Bucharest) for his help with the polarographic determinations.

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ANALYTICAL DATA

STUDY OF THE TAUTOMERIC FORMS OF 3,4-DIHYDROXYPHENYLACETIC ACID BY CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Summary—The pH-dependent ^{13}C chemical shifts indicate an approximately 1:1 ratio of the 3-OH:4-OH tautomeric forms of singly dissociated 3,4-dihydroxyphenylacetic acid. It is found that the ^{13}C chemical-shift method is an effective technique for determining tautomeric forms from pK values.

In recent years, there has been considerable interest in the potential use of nuclear magnetic resonance,[1,2] particularly carbon-13 nuclear magnetic resonance (^{13}C NMR), for characterizing the behaviour of amino-acids as a function of pH.[3,4] It is considered that ^{13}C NMR spectroscopy should be useful for studying details of the state of ionization of catechol derivatives, because the spectral responses of the individual carbon atoms are well separated. Recently, the microscopic acid dissociation constants (micro-constants) and the distribution of various ionic forms of 3,4-dihydroxyphenylpropionic acid and DOPA as a function of pH have been reported.[5] An attempt has been made to use the results to evaluate the ^{13}C NMR data to find the pK values and distribution of ionization states of several hydroxyphenyl compounds. On the basis of the pH-dependent ^{13}C chemical shifts, the ratio of the 3-OH and 4-OH tautomeric forms of 3,4-dihydroxyphenylacetic acid in basic solution has been calculated.

EXPERIMENTAL

Reagents and titration

3,4-Dihydroxyphenylacetic acid, 3-hydroxyphenylacetic acid, 4-hydroxyphenylacetic acid, 3-methoxy-4-hydroxyphenylacetic acid, and phenylacetic acid were dissolved in D_2O to give concentrations of 0.5–0.8M. The NMR sample was titrated directly with 10M potassium hydroxide solution in D_2O, under an atmosphere of CO_2-free nitrogen, at 35 ± 0.1°. The pD values were calculated according to the equation[6] pD = pH + 0.4 where pH is the pH-meter reading.

^{13}C NMR

Proton-decoupled ^{13}C chemical shifts were measured at 20 MHz on a Varian CFT-20 spectrometer operated in the pulsed Fourier transform mode. The probe temperature was 35 ± 2°. Dioxan (0.2%) was used as internal standard and the chemical shifts were converted to a ppm scale relative to dioxan (by using a conversion factor of 67.4 ppm).

Calculation of pK

The titration curves of 3,4-dihydroxyphenylacetic acid and its related compounds were analysed in terms of the chemical shift and the proton association equilibria by using a model equation of the form

$$\delta_{obsd} = \delta_{min} + \sum_{i=1,n} [\Delta_i 10^{(pH-pK_i)}]/[1 + 10^{(pH-pK_i)}] \quad (1)$$

where δ_{obsd} is the observed ^{13}C chemical shift, δ_{min} is the minimum chemical shift in the protonated form of 3,4-dihydroxyphenylacetic acid, and Δ_i and pK_i are the chemical shift and the dissociation constants, respectively, for the ith protonation transition.[7]

Determination of dissociation constants

The dissociation constants of compounds were calculated according to the method of the complementary tristimulus colorimetry (CTS method) which was reported in the previous paper.[8]

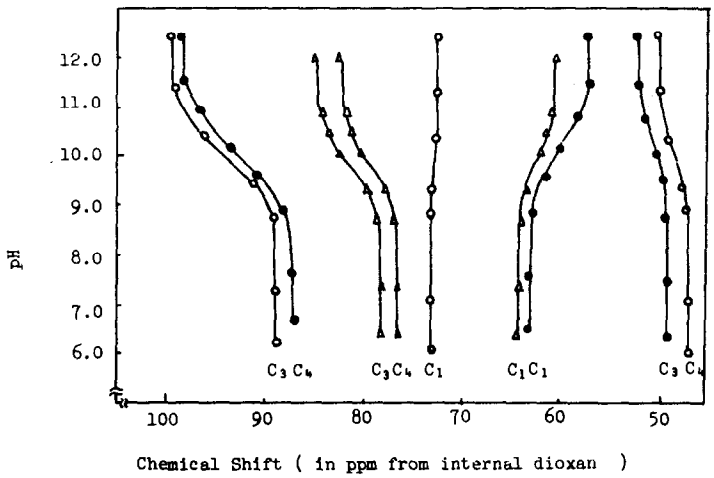
Determination of micro-constants

The acid dissociation equilibria of 3,4-dihydroxyphenylacetic acid may be expressed as shown in Chart I. The micro-constants were calculated by the method of Edsall *et al.*[9] which was employed previously in the calculation of micro-constants of 3,4-dihydroxyphenylpropionic acid and DOPA.[5] In scheme I, the dissociation constant of 3-methoxy-4-hydroxyphenylacetic acid was expediently used as substitution value of k_1, which corresponds to the dissociation of the *p*-phenol group.

RESULTS AND DISCUSSION

The chemical shifts of the carbon atoms (designated C-1, C-3, and C-4) of 3,4-dihydroxyphenylacetic acid and its related compounds were measured in D_2O solution at several pH values between 5 and 12. The relationship between pH and the chemical shifts of the compounds is shown in Fig. 1. The data were then fitted to equation (1).

In Table 1, the total shifts for C_O, C_α, C-1, C-3, and C-4 carbon atoms caused by the ionization of the phenolic hydroxy group are summarized and supplemented by the literature values[10] for other hydroxyphenyl compounds. Comparison of the results for C-1, C-3, and C-4 of 4-hydroxyphenylacetic acid, 3-methoxy-4-hydroxyphenylacetic acid, glycyl-L-tyrosylamide and glycyl-L-tyrosylglycine



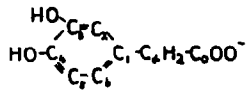


Fig. 1. ^{13}C Chemical shift for 3,4-dihydroxyphenylacetic acid and its related compounds as a function of pH, relative to dioxan as internal standard.

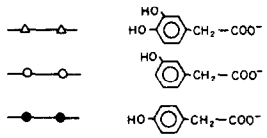


Table 1. ^{13}C NMR shifts for C_O, C_x, C-1, C-3, and C-4 in titration

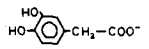
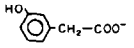
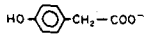
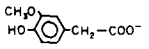
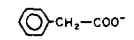
Compound	C_O	C_x	C-1	C-3	C-4
	4.4	4.0	3.3	7.4	6.6
	4.2	4.1	0.3	10.8	3.3
	4.1	4.0	5.9	3.1	10.4
	4.2	4.1	6.9	3.4	10.9
	4.0	4.2			
Glycyl-L-tyrosylamide[10]			6.2	3.3	10.4
Glycyl-L-tyrosylglycine[10]			6.2	3.3	10.4

Table 2. Dissociation constants of 3,4-dihydroxyphenylacetic acid and its related compounds

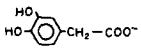
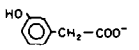
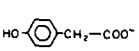
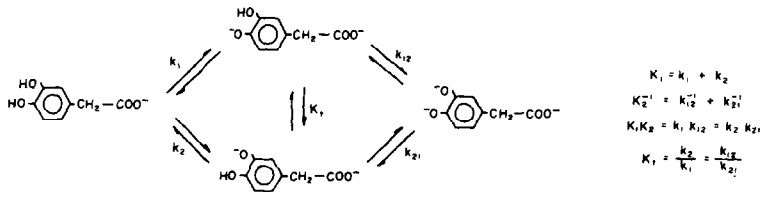
Compounds	Carbon atom	pK_1 (D_2O, 35°)	pK_2 (D_2O, 35°)	pK_1 (H_2O, 35°)	pK_2 (H_2O, 35°)	pK_1 (H_2O, 25°)	pK_2 (H_2O, 25°)
	C-1	9.78 ± 0.08					
	C-3	9.78 ± 0.06	11.49 ± 0.18	9.45 ± 0.02	11.88 ± 0.05	9.61 ± 0.04	12.03 ± 0.02
	C-4	9.80 ± 0.04	11.53 ± 0.11				
	C-1	10.11 ± 0.06					
	C-3	10.08 ± 0.07		9.92 ± 0.01		9.95 ± 0.03	
	C-4	10.00 ± 0.04					
	C-1	9.99 ± 0.06					
	C-3	9.87 ± 0.08		9.83 ± 0.02		9.96 ± 0.05	
	C-4	9.95 ± 0.09					

Table 3. Microscopic acid dissociation constants and tautomeric constant of 3,4-dihydroxyphenylacetic acid

Compound	pk_1	pk_2	pk_{12}	pk_{21}	K_t	Reference
	9.74*	9.76	11.59	11.57	0.96 (35°)	
	9.87	9.90	11.86	11.84	0.94 (25°)	5

[μ = 0.1 ($NaClO_4$)]

* Dissociation constant of 3-methoxy-4-hydroxyphenylacetic acid (9.74 ± 0.02).



Scheme I. Ionization equilibria of 3,4-dihydroxyphenylacetic acid.

shows that the ^{13}C chemical shifts of these carbon atoms are not influenced by the side-chain. The ^{13}C chemical shifts of 3,4-dihydroxyphenylacetic acid are the means of the shifts for 3-hydroxyphenylacetic acid and 4-hydroxyphenylacetic acid. This is considered to mean that the shifts for 3,4-dihydroxyphenylacetic acid correspond to an approximately 1:1 ratio of the 3-OH and 4-OH singly dissociated forms.[11] As can be seen from Table 1, the C-3 and C-4 shifts for 3-methoxy-4-hydroxyphenylacetic acid are practically the same as those for 4-hydroxyphenylacetic acid. If it is assumed that the C-3 shift for 3-methoxy-4-hydroxyphenylacetic acid is essentially the same as the C-3 shift in dissociation of the 4-hydroxy proton of 3,4-dihydroxyphenylacetic acid, two pK values could be calculated from equation (1). A similar argument can be considered for the C-4 shifts.

The pK values are given in Table 2 together with the standard deviations. Estimates of the pK values from the shifts for different carbon atoms agree fairly well with the values obtained at 35° in aqueous solution except for 3,4-dihydroxyphenylacetic acid for which the agreement is poorer. The tautomeric constant (K_t) and the micro-constants defined in Scheme I were calculated for a temperature of 35° and aqueous solution and the values are listed in Table 3. The micro-constants values are increased by 0.1–0.3 by a decrease of 10° in temperature.

In Table 3, the micro-constants k_1, k_{21}, k_2, and k_{12} previously obtained[5] are seen to agree reasonably with those calculated from the ^{13}C chemical shifts of C-4 and C-3 in D_2O solution of 3,4-dihydroxyphenylacetic acid. Thus the ^{13}C chemical shifts must be monitoring the effect of the micro-constants of the catechol derivatives.

The tautomeric constant was calculated to be 0.96 in aqueous solution and considered to be 1.04 in D_2O solution (C-3/C-4) and the ^{13}C chemical shifts give an intermediate value.

From these results, it is concluded that 3,4-dihydroxyphenylacetic acid dissociates the first phenolic proton from either the 3- or the 4-position with about equal probability; this agrees with the conclusion from the previous paper.[5]

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ANALYTICAL PROPERTIES OF BIPYRIDYLGLYOXAL BIS(4-PHENYL-3-THIOSEMICARBAZONE)

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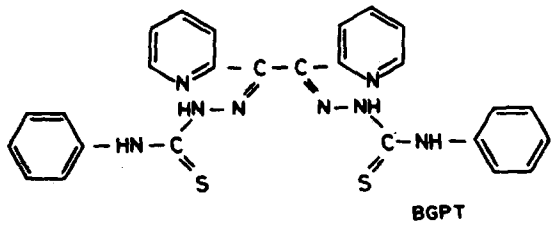
Summary—The synthesis and analytical properties of bipyridylglyoxal bis(4-phenyl-3-thiosemicarbazone) are described. The solubility, spectral characteristics and pK values are reported, as well as the absorptivity and stoichiometric ratio of metal chelates formed.

Some phenylthiosemicarbazones have been studied as reagents,[1–6] but compounds with the bis(phenylthiosemicarbazone) grouping have received very little attention. Ballschmiter[7,8] studied some derived from biacetyl and glyoxal, varying the phenyl substituent, but photometric applications have been not reported; biacetyl bis(4-phenyl-3-thiosemicarbazone) has been proposed for the selective determination of copper.[9]

In this paper, the physicochemical properties and analytical possibilities of bipyridylglyoxal bis(4-phenyl-3-thiosemicarbazone) (BGPT) are presented and compared with those of bipyridylglyoxal dithiosemicarbazone.



BGPT

EXPERIMENTAL

Preparation of reagent

Dissolve 2.12 g (0.01 mole) of bipyridylglyoxal and 3.34 g (0.02 mole) of 4-phenyl-3-thiosemicarbazide in 30 ml of ethanol and add 5 ml of concentrated hydrochloric acid. Reflux for 4 hr, and evaporate slowly until biphenylthiosemicarbazone precipitates. Filter off the yellow product, and recrystallize from ethanol–water (1:1) (m.p. 217–219°; yield, 20%). Found: C 53.0%, H 4.3%, N 19.3%. Calculated for $C_{26}H_{22}N_8S_2.2HCl$: C 53.52%, H 4.11%, N 19.19%.

Properties. Some physicochemical properties of BGPT are summarized in Table 1. Solutions of BGPT (0.1%) in ethanol and ethanol–water mixtures at different pH values were stable for more than a week. The absorption spectra of $9.0 \times 10^{-6}M$ BGPT in 2:3 ethanol–water solutions at various pH values are plotted in Fig. 1, showing bathochromic shifts in acid and alkaline media. Values of pK were calculated from the variation of absorbance with pH, by the Stenstrom and Goldsmith[10] and Sommer[11] methods. The pK values shown in Table 1 are the arithmetic mean of the values obtained from measurements at four different wavelengths.

The NMR spectrum of BGPT in dimethylsulphoxide shows a peak at 2.05 ppm which indicates the presence of an –SH group in small proportion, in equilibrium with the thione group.

Spectrophotometric study of reactions with metal ions. The reactions of 40 cations with BGPT were tested at different pH values. The most sensitive reactions were those of Co(II), Ni(II), Fe(II) and (III), Cu(II), Zn(II), Cd(II) and Mn(II). A spectrophotometric study of the chelates formed has been made. The solutions were prepared in 25-ml standard flasks with 1–5 ppm of metal ion, 5 ml of 0.1% solution of BGPT in ethanol, 5 ml of buffer solution and 10 ml of ethanol to prevent precipitation, and dilution with distilled water. The absorbance was measured at 350–700 nm, against reagent blanks. The most important results are summarized in Table 2.

RESULTS AND DISCUSSION

BGPT was prepared by a standard procedure involving the acid-catalysed reaction between the appropriate semicarbazide and α-dicarbonyl compound in ethanol or aqueous ethanol medium.[12,13]

The reagent show only two ionization steps. Since the molecule is symmetrical and the distance between the dis-

Table 1. Physicochemical properties of bipyridylglyoxal bis(4-phenyl-3-thiosemicarbazone)

Solubility in water, *g/l.*	0.1
Solubility in ethanol, *g/l.*	12.3
Solubility in dimethylformamide, *g/l.*	28.2
Solubility in chloroform, *g/l.*	0.2
Aromatic protons (NMR spectrum), *ppm*	7.1–9.0
–NH– (NMR spectrum), *ppm*	4.15
–SH (NMR spectrum), *ppm*	2.05
–NH–frequency, cm^{-1}	3200 w, 3090 w m
>C=N– frequency, cm^{-1}	1610 s, 1530 s
>C=S frequency, cm^{-1}	1090 m, 1030 w, 1.000 w
pK_1=pK_2 (Stenstrom and Goldsmith method)	3.27
pK_3=pK_4 (Stenstrom and Goldsmith method)	11.62
pK_1=pK_2 (Sommer method)	3.20
pK_3=pK_4 (Sommer method)	11.68

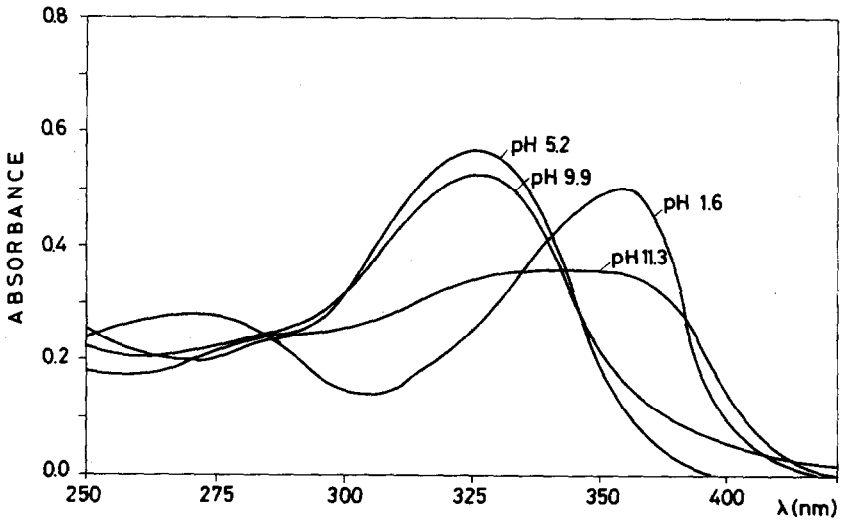


Fig. 1. Absorption spectra of $9.0 \times 10^{-6} M$ BGPT in 2:3 ethanol–water solution at various pH values.

sociable protons is relatively long, the values of the constants K_1 and K_2 and also K_3 and K_4 would be expected to lie close together, and are not distinguishable by spectrophotometry. The ionization steps are, therefore:

$$H_4L^{2+} \overset{K_1 \sim K_2}{\rightleftharpoons} H_2L \overset{K_3 \sim K_4}{\rightleftharpoons} L^{2-}$$

The nitrogen atom in the pyridine ring can be protonated, and the compound acts as a weak base; the value found resembles the corresponding constants of pyridine compounds.[14] The final dissociation is due to loss of the proton of the –SH group.[15]

BGPT is unstable towards strong oxidizing agents, but stable in the presence of reducing substances, and it is not hydrolysed by acids, and can be used in acidic solutions.

The reagent acts as a tetradentate ligand with convenient steric arrangement of its donor groups in the complexes formed with Zn(II), Cd(II) and Cu(II) (1:1 stoichiometric ratio) in a similar manner to other *vic*-dithiosemicarbazones. In the case of the complexes of Fe(II), Co(II) and Ni(II) the stoichiometric ratios (1:2 and 2:3, metal ion–BGPT) indicate that each half of the molecule behaves independently; these complexes are similar to the complexes of picolinaldehyde thiosemicarbazone and related compounds.[16,17]

The analytical possibilities of BGPT are superior to those of bipyridylglyoxal dithiosemicarbazone, owing to the higher molar absorptivities of the chelates and to the shift of the absorption peaks towards longer wavelengths; moreover, the BGPT chelates can be extracted more easily into benzene, toluene and chloroform. The introduction of the phenyl radical at the end of the thiosemicarbazide molecule is an excellent example of how group action in organic compounds can be modified to provide increased sensitivity.

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Table 2. Characteristics of bipyridylglyoxal bis(4-phenyl-3-thiosemicarbazone) compounds

Ion	Buffer, pH	Colour	λ, nm	ε, $l.mole^{-1}.cm^{-1}$	M:R
Ag(I)	5.0	yellow (ppte)			
Pb(II)	9.5	yellow	390	2.86×10^4	1:1, 1:3
Hg(I)	5.0	yellow (ppte)			
Hg(II)	5.1	yellow	370	2.53×10^4	1:1, 1:2
Cu(II)	2.2	yellow	420	9.2×10^3	2:1
Cu(II)	8.7	yellow	380	3.40×10^4	1:1, 2:1
Cd(II)	9.3	yellow	385	4.61×10^4	1:1
Bi(III)	5.5	yellow	390	1.83×10^4	1:2
Pd(II)	5.7	yellow	380	2.04×10^4	2:3
Pt(IV)	5.0	yellow			
Au(III)	5.0	yellow			
Fe(II)	2.0	violet red			
Fe(II)	5.5	green	640	7.9×10^3	1:2
Fe(III)	5.0	yellow			
V(V)	5.0	yellow			
Mn(II)	9.5	yellow	390	4.20×10^4	1:3
Ni(II)	6.3	yellow	370	3.37×10^4	2:3
Zn(II)	8.9	yellow	390	4.32×10^4	1:1
Co(II)	1.4	yellow	420	1.79×10^4	2:3
Co(II)	5.3	yellow	390	3.28×10^4	2:3

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ANNOTATION

REMARQUES SUR LE MICRODOSAGE DU BORE ET DU GERMANIUM DANS LES COMPOSES ORGANIQUES ET MINERAUX

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Résumé—La destruction par voie humide en micromatras du type Kjeldahl associée à une méthode de dosage par colorimétrie spectrophotométrique avec emploi d'azométhine H, la combustion en bombe de Parr sous pression d'oxygène, l'attaque par le peroxyde de sodium associées au dosage acidimétrique de l'acide mannitoborique ont été étudiées pour le microdosage du bore dans les composés organiques et minéraux complémentairement à la méthode de combustion dans l'oxygène en fiole de Schöniger, antérieurement mise en oeuvre, qui convient mal dans le cas des composés minéraux; c'est la destruction en micromatras qui est généralement utilisée comme méthode complémentaire. Des techniques de destruction analogues, associées au dosage acidimétrique de l'acide mannitogermanique ou à une méthode de colorimétrie spectrophotométrique avec emploi de phénylfluorone, ont été essayées pour le microdosage du germanium ainsi que le dosage gravimétrique de GeO_2 mais aucune n'est entièrement satisfaisante, les unes manquent d'universalité et les autres de précision.

La méthode de combustion dans l'oxygène en fiole de Schöniger mise en oeuvre dans notre laboratoire pour la microanalyse élémentaire des substances organiques borées[1] est mise en défaut lorsqu'elle est appliquée à des composés tels que borures, boronitrures, carbures de bore et autres substances minérales en vue du dosage microanalytique du bore, même lorsqu'on ajoute au prélèvement analytique des réactifs tels que carbonate ou perchlorate de potassium, peroxyde de sodium *etc.*

En vue de permettre ce dosage microanalytique du bore, dans lesdits composés, nous avons essayé une autre méthode comportant une attaque "micro-Lorenz" modifiée, en micromatras du type Kjeldahl[2] associée à un mesurage final par colorimétrie spectrophotométrique avec emploi d'azomethine.[3] En effet la solution obtenue après attaque est trop acide pour permettre, comme dans notre précédent travail, un dosage précis de l'acide mannitoborique.[1] Les résultats obtenus dans le cas du carbure de bore restant cependant très déficitaires, d'autres méthodes comportant soit une combustion en bombe de Parr[4] sous pression d'oxygène soit une attaque par le peroxyde de sodium dans une microbombe de Würzschmitt[5] ont été expérimentées, mais également sans succès, tout au moins pour le microdosage du bore dans cette substance; par contre elles sont utilisables dans le cas des substances organiques borées. La bombe spéciale de Gradskova et Bondarevskaya[6] employée ailleurs pour minéraliser par le peroxyde de sodium 30 à 40 mg de composé organique silicié et boré n'a pas été essayée.

Le dosage du germanium a antérieurement fait l'objet de plusieurs publications.[7,8] Nous avons essayé l'application au dosage microanalytique du germanium des méthodes que nous avions déjà mises en oeuvre dans le cas du bore ainsi que la méthode comportant une calcination en creuset du prélèvement analytique et un dosage gravimétrique.

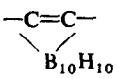
PARTIE EXPERIMENTALE

Bore

Attaque du type micro-Lorenz modifié

(*a*) *Méthode applicable aux substances minérales borées à l'exception du carbure de bore.* La masse du prélèvement analytique est réduite de quelques milligrammes à moins d'un milligramme en fonction de la teneur en bore. Le mode opératoire que nous avons antérieurement décrit pour le dosage microanalytique du titane dans les substances minérales[2] doit être légèrement modifié comme suit en vue de son application au cas du bore afin d'éviter une perte d'acide borique: les ébullitions sont très douces et ne sont maintenues que pendant 10 minutes; la quantité d'eau oxygénée est doublée (8 gouttes) et l'ébullition en présence d'eau est supprimée.

(*b*) *Méthode applicable aux substances organiques borées.* L'application du mode opératoire ci-dessus, donne lieu à l'obtention de résultats très déficitaires lors de l'analyse de certaines substances organiques contenant par exemple le groupe



Il convient de revenir au mode opératoire mis en oeuvre pour le microdosage du titane dans les substances organiques[2] en le modifiant comme suit: les ébullitions sont très douces et ne sont maintenues que pendant 10 minutes; la quantité d'eau oxygénée employée est légèrement augmentée (4 à 5 gouttes). Une quatrième addition est effectuée s'il reste encore des vapeurs nitreuses. L'addition d'eau bouillante est supprimée.

Attaque en bombe sous pression d'oxygène[4]

Cette méthode étudiée en vue du microdosage du carbure de bore, pour lequel elle ne convient finalement pas, est cependant applicable aux substances organiques; une bombe de Parr à oxygène (AC 5E) a une capacité (22 ml) suffisante à cette fin. L'emploi d'une bombe de 340 ml n'améliore pas les résultats de dosage du bore dans le carbure de bore.

Les conditions expérimentales sont les suivantes: un prélèvement de 0,5 à 4 mg de substance (selon la teneur en bore) est pesé dans une cupule de platine d'environ 10 mm de diamètre, 2 mm de hauteur et 0,2 mm d'épaisseur, garnie d'environ 10 mg de petits copeaux de paraffine ($F = 52$–$54°$). La substance est recouverte de 10 à 20 mg de petits copeaux de paraffine et de 10 à 20 mg d'hydroxyde de sodium solide qui peut être sous forme d'amiante sodé (ascarite). La cupule est introduite dans la bombe et la pression d'oxygène amenée à 30 bars. L'allumage est effectué par l'intermédiaire d'un fil de coton. Après combustion, la cupule et les eaux de rinçage de la bombe sont placées dans un Erlenmeyer rodé. La solution est neutralisée par de l'acide sulfurique puis traitée comme après combustion en fiole de Schöniger[1] (légère acidification, ébullition au reflux, dosage acidimétrique du complexe mannitoborique avec détection du point équivalent par pH-métrie avec une électrode de verre).

Attaque par le peroxyde de sodium en microbombe de Würzschmitt[5]

Cette méthode s'applique aux mêmes produits que la précédente. Le mode opératoire est classique (emploi de 2 à 3 gouttes d'éthylène glycol pour l'amorçage mais de seulement 500 mg de peroxyde de sodium pour permettre le dosage ultérieur de l'acide mannitoborique avec une précision suffisante).

Après ébullition dans des béchers de silice fondue pour détruire l'eau oxygénée, la solution est neutralisée puis traitée et dosée comme après combustion en fiole de Schöniger.

Dosage de l'acide borique par colorimétrie spectrophotométrique

Le dosage colorimétrique de l'acide borique avec emploi d'azométhine H est applicable après une attaque du type micro-Lorenz. L'azométhine H est préparé selon la méthode de Shanina *et al.*;[3] le réactif ainsi obtenu est stable pendant plusieurs années. Ce réactif se trouve maintenant sur le marché (Pierce, Box 117, Rockford, Illinois 61105, USA) mais le produit commercial n'a pas été essayé dans notre laboratoire. La solution obtenue après attaque est transvasée quantitativement soit directement dans la fiole jaugée de 100 ml où sont ajoutés les réactifs nécessaires à la colorimétrie soit dans une fiole intermédiaire d'où sont effectués des prélèvements aliquotes.[2] En effet afin que la loi de Lambert–Beer soit suffisamment suivie il est nécessaire que la concentration finale en bore soit inférieure à 1 µg/ml. Les réactifs et le mode opératoire sont ceux de Shanina *et al.*;[3] toutefois avant l'addition de solution tampon (pH 5,2) nous amenons le pH à 3–3,8 par addition d'ammoniaque, en contrôlant sa valeur à la touche sur du papier indicateur. Les réactifs utilisés pour l'attaque ont peu d'influence. Il est toutefois préférable de tenir compte du "blanc de solution d'attaque";[2] à cette fin, nous effectuons des attaques en l'absence de substance à analyser et introduisons une partie aliquote ou la totalité des solutions ainsi obtenues dans les fioles de colorimétrie où sont préparées les "solutions étalons"[2] (standard solution de Shanina *et al.*[3]) contenant une quantité connue de bore (sous forme de solution titrée d'acide borique). Ainsi toutes les fioles de colorimétrie contiennent les mêmes quantités de réactifs traités de la même façon.

Shanina *et al.*[3] ainsi que Capelle[9] ont étudié l'influence de la présence simultanée de divers autres éléments sur ce dosage colorimétrique du bore. Au fur et à mesure que les problèmes se sont présentés nous avons étudié l'influence des éléments dont la liste est rapportée ci-après, leur teneur étant de l'ordre de grandeur de quelques dixièmes de milligrammes par 1 ou 2 mg de prélèvement analytique; c'est ainsi qu'il est apparu que As, Br, Ca, Cd, Cl, I, Mg, Mn, N, Na, P, Rb, S, Sn ne gênent pas tandis que Bi, Hg, Nb, Ti, Se gênent le dosage du bore. Seule l'élimination de l'influence gênante de Ti(IV) a été étudiée. Pour éliminer cette influence, nous masquons Ti(IV) en le complexant par addition de 10 ml de solution 0,2*M* de sel disodique de l'acide éthylènediaminetétraacétique dans toutes les fioles de colorimétrie; en outre nous introduisons également une solution de Ti(IV) dans les solution étalons de telle sorte que la concentration en titane y soit du même ordre de grandeur que dans les fioles contenant la solution à doser. La concentration finale en titane doit rester inférieure à 1,5 µg/ml.

Germanium

Calcination et gravimétrie

La calcination en creuset de platine[10] (l'emploi de creuset de silice, dont la pesée est moins précise, donne des résultats moins reproductibles) en présence de 2 gouttes d'acide sulfurique 6*N* puis de 2 gouttes d'acide nitrique 15–16*N* (l'addition d'acide nitrique étant éventuellement répétée 2 ou 3 fois jusqu'à obtention d'un poids constant), permet de peser l'oxyde GeO_2. La méthode est simple; sa fiabilité est accrue lorsque l'acide sulfurique est introduit en premier lieu: le sulfate de germanium initialement formé se transforme en dioxyde vers 200°. Toutefois cette méthode n'est pas universelle et ne convient pas pour l'analyse de nombreuses substances (liquides volatils, substances contenant simultanément un élément laissant également un résidu de calcination).

Combustion en fiole de Schöniger et dosage acidimétrique

Il est possible de doser le germanium dans les substances organiques en appliquant le même principe et le même mode opératoire que pour le microdosage du bore:[1] le germanium est finalement dosé par titrage acidimétrique de l'acide mannitogermanique avec détection pH-métrique, par électrode de verre, du point final de titrage.

Il est toutefois préférable, dans le cas du germanium, de garnir le fond de la fiole de Schöniger avec un liquide absorbeur légèrement basique (10 ml d'eau + quelques milligrammes d'hydroxyde de sodium solide). Bien que Shanina *et al.*[11] recommandent l'emploi de spirales de silice nous continuons à placer l'échantillon dans un support de platine comme Obtemperanskaya *et al.*[12] Lors de l'emploi du support de silice, d'ailleurs trop fragile pour une utilisation courante, les combustions sont, en effet, souvent incomplètes (dépôts de charbon).

La masse atomique du germanium étant environ 7 fois plus élevée que celle du bore, le coefficient de calcul de la teneur en germanium à partir du volume de réactif titrant et de la masse du prélèvement analytique est également 7 fois plus élevé que dans le cas du bore ainsi que les erreurs absolues pouvant entacher les résultats d'analyse; en contre-partie il n'est pas possible d'élever la masse des prélèvements analytiques au-delà de 1,5 mg.

Par ailleurs, le dosage acidimétrique du germanium sous forme d'acide tritirongermanique n'est pas plus précis.[13] Quant au dosage complexométrique de Ge(IV) par le tiron[14] sa précision est insuffisante.

En outre, nous avons rencontré des difficultés lors de la préparation de la solution titrée de dioxyde de germanium en vue de l'étalonnage de réactif titrant (hydroxyde de sodium) ou de la préparation de solutions étalons pour la colorimétrie. Certains lots de dioxyde de germanium se dissolvent facilement, à chaud, dans de l'ammoniaque 1*N*

(la solution ainsi obtenue est ensuite diluée) d'autres ne se dissolvent pas. Lorsqu'un peu d'eau oxygénée ne gêne pas lors du dosage final du germanium en solution (par colorimétrie avec emploi de phénylfluorone, par exemple) il est possible de dissoudre du germanium pur à 99,999% dans de l'eau oxygénée à 3% sous agitation pendant quelques heures (la solution ainsi obtenue est ensuite diluée).

Attaque du type micro-Lorenz modifié

Nous n'avons pas essayé plusieurs méthodes de digestion par voie humide passées en revue par Belcher *et al.*[15] car nous les avons jugées trop compliquées. L'attaque du type micro-Lorenz modifiée, mise en oeuvre dans notre laboratoire pour le microdosage colorimétrique du germanium sous forme de germanomolybdate[16] nous a conduits à des résultats très déficitaires. Nous avons essayé sans succès plusieurs variantes (modification durées d'ébullition, des quantités d'acide, addition de réactifs tels que permanganate de potassium, persulfate de potassium). Bien que la colorimétrie du germanomolybdate[16] mise en oeuvre ne soit guère satisfaisante si l'on ne prend pas des précautions particulières, comme l'indiquent Kitson et Mellon[17] ou Chalmers et Sinclair,[18] elle ne peut être rendue responsable des déficits observés.

Attaque en bombe sous pression d'oxygène et dosage acidimétrique

Il est possible de doser le germanium dans les substances organiques en appliquant le même mode opératoire que pour le microdosage du bore. La précision reste mauvaise comme dans le cas de la méthode en fiole.

Attaque par le peroxyde de sodium en microbombe de Würzschmitt

L'emploi du peroxyde de sodium diminuant la sensibilité du dosage acidimétrique de l'acide mannitogermanique, il est nécessaire de faire appel à une autre méthode de dosage. Une méthode colorimétrique (mesure à 520 nm—attente de 2 h) avec l'emploi de phenylfluorone, selon Obtemperanskaya *et al.*,[12] est applicable après attaque en bombe de façon classique (emploi de 3 g de peroxyde de sodium) sous réserve d'effectuer les opérations ci-après: la solution obtenue après attaque et lavage des bombes est portée à ébullition jusqu'à ce que son volume soit réduit à une vingtaine de ml afin d'éliminer la majeure partie de l'eau oxygénée; l'hydroxyde de sodium formé est neutralisé avec 10 ml d'acide chlorhydrique $6N$; la solution est filtrée; des parties aliquotes sont prélevées de telle sorte que la concentration finale en germanium ne dépasse pas 0,8 µg/ml; des attaques sans introduction de substance à analyser ("blanc de solution d'attaque"[2]) sont effectuées; des prélèvements aliquotes de "blanc de solution d'attaque" sont introduits, dans les fioles de colorimétrie où sont préparées les solutions étalons[2] contenant une quantité connue p de germanium introduit sous forme de solution titrée.

Ainsi toutes les fioles de colorimétrie contiennent les mêmes quantités de réactifs traités de la même façon. La colorimétrie est effectuée sans recours à une courbe d'étalonnage: son usage est remplacé par celui de solutions étalons dont on mesure l'absorbance d. La quantité inconnue P de germanium (absorbance D) est calculée à partir de p par une simple règle de proportionnalité d'après la formule

$$P = \frac{pD}{d}$$

Les résultats obtenus pour le dosage des substances organiques sont souvent déficitaires même si on ajoute 1 goutte de pyridine (réactif recommandé pour la minéralisation en bombe du sélénium[20]) aux 2 gouttes d'éthylène glycol. Par contre des résultats valables sont obtenus pour le dosage de composés minéraux contenant simultanément U, Na, K ou quelques unités pour cent de Cu, Ca ou Ba.

RESULTATS

Quelques résultats représentatifs sont portés dans les tableaux 1, 2, 3, 4. D'autres substances ont été analysées avec succès mais leur nombre est resté limité aux substances

Tableau 1. Microdosage du bore dans les substances organiques

Méthode	Composé	Masse du prélèvement, *mg*	Teneur en bore, %	
			Calculée	Trouvée
"Micro-Lorenz" modifié (procédé *b*)	Diphénylborinate d'aminoéthyle	4,036	4,81	5,0
		4,944		4,9
		5,310		5,0
		5,521		4,8
	Anhydride *p*-tolylboronique	2,239	9,17	8,8
		2,475		9,2
		3,867		9,3
		1,837		8,9
		1,516		9,1
		1,660		9,3
Attaque en bombe sous pression d'oxygène	Diphénylborinate d'aminoéthyle	3,868	4,81	5,0
		1,047		4,7
		1,086		4,7
	Anhydride *p*-tolylboronique	0,939	9,17	8,7
		1,072		9,1
		1,006		9,1
		1,270		9,2
Attaque en bombe par le peroxyde de sodium	Anhydride *p*-tolylboronique	4,275	9,17	9,2
		3,705		8,9
		5,084		9,2

Tableau 2. Microdosage du bore dans le diborure de titane

Méthode	Masse du prélèvement, *mg*	Teneur en bore, %	
		Calculée*	Trouvée
"Micro-Lorenz" modifié (procédé *a*)	0,978	31,1	29,9
	0,786		31,0
	0,820		30,2
	0,840		30,0
	0.670		29,9
	0,839		29,8
	0,745		30,9
	0,541		30,5
	0,781		30,0
	0,893		31,3
	0,708		29,7
	0,802		29,9

*D'après le fournisseur, ce produit n'est pas absolument pur. En tenant compte de la valeur minimale garantie par le fournisseur (30%) et du dosage du titane effectué dans notre laboratoire, on peut considérer que la teneur en bore est comprise entre 30,0 et 30,8%.

Tableau 3. Microdosage du germanium dans les substances organiques

Méthode	Composé	Masse du prélèvement *mg*	Teneur en germanium, %	
			Calculée	Trouvée
Calcination et gravimétrie	Tetraphénylgermane	2,848	19,05	19,0
		3,062		19,8
		2,771		19,1
		3,049		19,2
		2,625		18,9
	Triphénylallylgermane	4,994	21,05	20,9
	Triphénylisopropylgermane	3,238	20,92	21,0
Combustion en fiole à oxygène	Triphénylisopropylgermane	2,446	20,92	21,3
		1,920		20,5
		2,006		20,2
		1,720		20,5
		1,800		21,1
		1,796		20,9
	Triphénylgermane	2,320	23,81	23,8
		1,656		24,9
		2,909		23,8
		2,310		23,5
		2,964		23,5
		2,567		24,3
		1,772		23,5
Attaque en bombe sous pression d'oxygène	Triphénylisopropylgermane	1,957	20,92	21,2
		2,005		21,0
		3,060		21,5
		6,839		21,4
	Triphénylgermane	4,650	23,81	23,7
		1,965		23,9
		2,430		23,2
		1,347		23,3
		1,511		24,5

Tableau 4. Microdosage du germanium dans les substances minérales

Méthode	Composé	Masse du prélèvement, *mg*	Teneur en germanium, % Calculée	Trouvée
Attaque en bombé par le peroxyde de sodium	Composé de recherches A (contenant U, Ge, H, O)	4,972	10,19	10,0
		4,872		10,1
		4,838		10,1
		4,505		10,3
		4,300		10,1
		5,408		10,1
		4,288		10,1
	Composé de recherches B (contenant U, Ge, Na, H, O)	2,940	17,3	16,7
		3,015		17,0
		3,040		16,8

dont nous disposions. Les résultats obtenus pour le carbure de bore, tous déficitaires quelle que soit la méthode mise en oeuvre, ne sont pas portés dans ces tableaux.

DISCUSSION ET CONCLUSIONS

Bore

Bien que les attaques en bombe sous pression d'oxygène, en bombe par le peroxyde de sodium, par voie humide (méthode "micro-Lorenz" modifiée) conviennent pour de nombreuses substances organiques, la combustion en fiole de Schöniger reste préférable car elle est plus simple et dans certains cas plus précise (diminution de la sensibilité du titrage provoquée par le peroxyde de sodium). Le dosage des liquides est amélioré et simplifié grâce à l'emploi de sachets de terphane[21] enveloppés dans du papier filtre sans cendres au lieu de capsules de gélatine.

L'attaque du type micro-Lorenz modifiée, en micro-matras de Kjeldahl, associée au dosage par colorimétrie spectrophotométrique avec emploi d'azométhine H est recommandée pour de nombreuses substances minérales (à l'exception du carbure de bore) bien que ce procédé reste délicat à mettre en oeuvre: un chauffage insuffisant conduit en effet à des résultats erronés par défaut (attaque incomplète) de même qu'un chauffage trop prolongé (pertes d'acide borique). Il convient de placer, comme témoins, sur la rampe de minéralisation deux substances-types qui sont traitées comme les substances inconnues et qui permettent de contrôler d'après les résultats de dosage du bore que le chauffage a été correct.

Germanium

Aucune des méthodes essayées n'est entièrement satisfaisante. Pour le dosage des substances organiques germaniées la calcination en creuset avec dosage gravimétrique manque d'universalité, la combustion en fiole de Schöniger ou en bombe sous pression d'oxygène associée au dosage acidimétrique de l'acide mannitogermanique manque de précision, les attaques par voie humide par une méthode du type micro-Lorenz modifiée ou les attaques en bombe par le peroxyde de sodium ne conviennent pas. Pour le dosage de substances minérales, l'attaque en bombe par le peroxyde de sodium associée à un dosage par colorimétrie spectrophotométrique en presence de phénylfluorone peut convenir.

L'étude de l'universalité des méthodes est en outre gênée par des difficultés d'approvisionnement en substances-types pures et stables.

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Summary—A wet destruction in a Kjeldahl flask followed by spectrophotometric measurement with azomethine H as reagent, combustion in oxygen in a Parr bomb, and destruction by heating with sodium peroxide followed by acidimetric titration of the mannitol–boric acid complex have been tested for the microdetermination of boron in organic and inorganic compounds and compared with the Schöniger-flask method, which fails to give good results in the case of inorganic compounds; the wet-combustion method is the most useful. Similar techniques, combined with the acidimetric titration of the mannitol–germanic acid complex, or spectrophotometric measurement using phenylfluorone as a complexing reagent, or gravimetric determination as GeO_2, have been tested for the microdetermination of germanium, but none of them is entirely satisfactory, for reasons of lack of either universality or precision.

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SPECTROPHOTOMETRIC DETERMINATION OF THE PSEUDOHALIDE 1,2,3,4-THIATRIAZOL-5-THIOLATE ION, $CS_2N_3^-$

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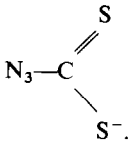
Summary—A critical study of the analytical methods available for the $CS_2N_3^-$ ion is reported. A modification of the argentimetric method is proposed. An oxidative study gave evidence of various steps corresponding to incompletely oxidized intermediates. The absorption maximum of the 1,2,3,4-thiatriazol-5-thiolate ion at 313 nm, with molar absorptivity of 7.4×10^{-3} l.mole^{-1}.cm^{-1} is utilized to develop a new analytical method. The spectrophotometric procedure is rapid and free from interference by many ions. A value of 1.51 ± 0.02 was found for pK of HCS_2N_3 at an ionic strength of 1.00M and at 25°. The spectrum of $CS_2N_3^-$ is changed by increasing acidity of the medium, due to the formation of HCS_2N_3; an isosbestic point is observed at 251 nm.

The $CS_2N_3^-$ ion, formed by reaction of carbon disulphide with aqueous sodium azide[1] is characterized as a pseudohalide[2,3] with the structure



Whereas at one time this ion was studied in relation to the catalytic role of carbon disulphide in the oxidation of azide ions by iodine,[4,5] current studies are directed toward its complexing properties.[6] Recent investigations indicate that it has an organic heterocyclic structure;[7–9] thus the former name azidodithiocarbonate has been changed to 1,2,3,4-thiatriazol-5-thiolate ion.

Although the preparation and storage of aqueous standard solutions of the sodium salt have been described,[10] a rapid method for determination of $CS_2N_3^-$ is not available. In this communication the spectral characteristics of the ion are utilized to develop a rapid, simple and sensitive method for its determination.

EXPERIMENTAL

Reagents

All reagents were of analytical grade unless otherwise specified, and distilled water was used throughout. Sodium azide[6] and carbon disulphide[11] were purified as described in the references cited. Standard solutions of $NaCS_2N_3$ were prepared as described earlier.[10,12]

Procedure

Modified Volhard method.[13] This procedure is suitable for 0.1M solutions. A sample of 15–25 ml is transferred to a 250-ml beaker. After addition of 40 ml of water and 2 ml of 6M nitric acid the sample is treated with a measured excess (at least 10 ml) of silver nitrate solution. The mixture is kept in the dark for at least 90 min. Then 10–15 ml of nitrobenzene and 1 ml of 40% ferric alum solution are added and the excess of silver is titrated with ammonium thiocyanate solution.

Spectrophotometric determination. Beer's law plots were prepared with solutions diluted from the 0.1M standard solution.

RESULTS AND DISCUSSION

Silver nitrate methods

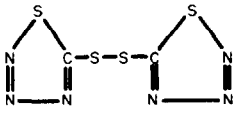
The classical Volhard method has been used by Browne and Smith[13] for the determination of $CS_2N_3^-$ ion, but long digestion with excess of silver and filtration were required. Potentiometric measurements with a silver electrode show that the solubility product of $AgCS_2N_3$ is about 10^{-11} mole^2/l.^{2}, intermediate between those for AgCl and AgSCN. Thus the precipitate will react with thiocyanate during the back-titration unless filtration or the nitrobenzene modification is used.

Oxidative titrations

The oxidation of $CS_2N_3^-$ to $(CS_2N_3)_2$ with iodine has been studied by Browne,[13] Feigl[14] and Solenkiand;[15] in spite of the apparently favourable standard potential[16] of +0.275 V for $(CS_2N_3)_2/CS_2N_3^-$, the titration is not quantitative. Complex ions such as $I_2CS_2N_3^-$ or $(CS_2N_3)_3^-$ may be formed and will markedly alter the potential-systems. Other mild oxidants such as iron(III) or ferricyanide are even less satisfactory.

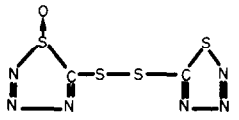
The use of strong oxidants leads to oxidation far beyond the disulphide $(CS_2N_3)_2$. Browne[17] suggested that species such as $CS_2N_3O^-$ and $CS_2N_3O_3^-$ might be formed as intermediates by direct oxidation or disproportionation of the pseudo-halogen in alkaline medium. In the direct oxidation with permanganate

(in excess) in acid medium, the first step is formation of $(CS_2N_3)_2$ (I), which precipitates.

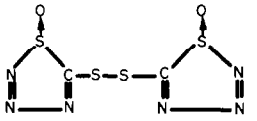


(I)

This precipitate reacts readily with excess of permanganate and dissolves, probably because of introduction of oxygen atoms into (I). The products could be the sulphoxides (II) and (III), or an ionic product $OCS_2N_3^-$.

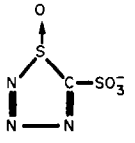


(II)

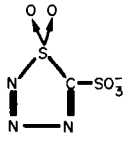


(III)

After this step, excess of permanganate reacts very slowly. There would be an overall 8-electron reaction if the ion (IV) (analogous to perchlorate or periodate) is formed, and an overall 10-electron reaction to give the sulphone (V):



(IV)



(V)

However, (IV) and (V) would be unstable unless stabilized by complex formation with "hard" type cations. Most probably there would be hydrolysis and cleavage of the ring structure with the possibility of continuing oxidation. A 12-electron change would result from the overall reaction:

$$CS_2N_3^- + 8H_2O \rightarrow N_2 + 2SO_4^{2-} + 15H^+ + HCN + 12e^-$$

If hydrogen cyanide is not removed, it can undergo slow hydrolysis and an additional 2-electron oxidation may occur, resulting in an overall 14-electron process:

$$HCN + 2H_2O \rightarrow NH_4^+ + CO_2 + H^+ + 2e^-$$

Permanganate in alkaline medium is able to oxidize ammonia to nitrogen, giving an additional 3-electron process. An overall 17-electron change is thus achieved:

$$CS_2N_3^- + 22OH^- \rightarrow CO_3^{2-} + 2SO_4^{2-} + 3/2N_2 + 11H_2O + 17e^-$$

Table 1 summarizes the results from an extensive study with several strong oxidizing agents in excess, followed by back-titration. Reactions corresponding to 8, 10, 12 and 14-electron changes were found in agreement with some of the intermediates mentioned above, but not with the precision and reliability required for analytical purposes. Good results (for the 17-electron reaction) were obtained only with alkaline permanganate (followed by acidification and back-titration), but the procedure is too cumbersome for the determination of the ion.

Spectrophotometric method

Spectral characteristics. In aqueous solution the spectrum of the 1,2,3,4-thiatriazol-5-thiolate ion is characterized by a maximum at 313 nm and a shoulder at 220–240 nm. Figure 1 shows the ultra-

Table 1. Stoichiometry of the reaction of $CS_2N_3^-$ (0.01*M*) with excess of strong oxidizing agents

Oxidizing agent	No. of electrons used in reaction*	Remarks
$K_2Cr_2O_7$ 0.017*M*	7.96	20–50% excess of titrant, in 2*M* HCl at 45°; addition of KI after 1 hr and back-titration of the released iodine with thiosulphate
Chloramine-T 0.1*M*	11.3	as above
$Br_2(BrO_3^-/Br^-)$ 0.2*M*	10.4	as above, at room temperature (24–28°)
$Ce(SO_4)_2$ 0.1*M*	8.2	as above, at room temperature (24–28°)
I_2 0.005*M*	14.5	20–50% excess of reagent in strongly alkaline medium (NaOH > 1*M*), during 40 min; then acidification and excess of iodine titrated with thiosulphate
$KMnO_4$ 0.02*M*	12.1	50–100% excess of reagent in 3*N* sulphuric acid at 40°, for 5 min; then KI added and the iodine formed titrated
$KMnO_4$ 0.02*M*	17.0	at least 200% excess of reagent in strongly alkaline medium (NaOH > 1*M*) for 20 min at room temperature; then acidification, KI added and iodine titrated with thiosulphate
$KMnO_4$ 0.1*M*	17.3	20–50% excess of reagent in strongly alkaline medium at 40° in presence of Ba^{2+} and after 20 min back-titrated with sodium formate

* From average results of at least 4 determinations.

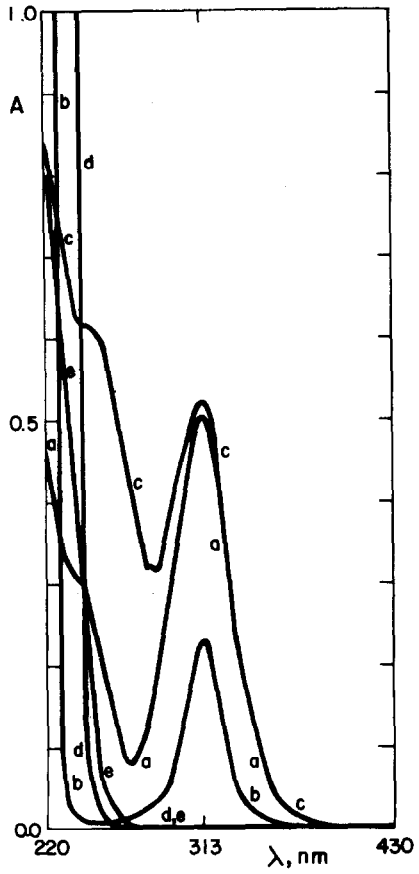


Fig. 1. Ultraviolet spectra of aqueous solutions of (a) $NaCS_2N_3$, $7.6 \times 10^{-5}M$; (b) CS_2, $9.2 \times 10^{-4}M$; (c) $(CS_2N_3)_2$, $7.6 \times 10^{-5}M$; (d) NaSCN, $1.0 \times 10^{-3}M$; (e) NaN_3, $1.0 \times 10^{-3}M$.

violet spectrum together with those of azide, thiocyanate, di(1,2,3,4-thiatriazol-5-yl)disulphide and carbon disulphide.

The molar absorptivity of $CS_2N_3^-$ in aqueous solutions at 313 nm is $(7.37 \pm 0.07) \times 10^3$ l.mole^{-1}.cm^{-1} (95% confidence limits).

Beer's law is obeyed over the transmittance range 15–65% and a Ringbom plot shows 3–20 μg/ml to be the optimum range for determination of $CS_2N_3^-$. The determination limit (90% transmittance) calculated from Beer's law, is 0.072 μg/ml.

Bathochromic shifts are found when solvents less polar than water are used. Thus λ_{max} changes to 321 nm in ethanol and 323 nm in acetonitrile, and the maximum absorbance increases 6% and 15% respectively, relative to aqueous medium. The observed shift in λ_{max} and the enhancement suggest an $n \rightarrow \pi^*$ transition,[18] although the molar absorptivity appears too high. Probably $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions occur simultaneously. The spectral pattern of $CS_2N_3^-$ in water is similar to that of carbon disulphide, but the molar absorptivity at 313 nm is 50 times as great. This leads to a spectrophotometric method for the determination of carbon disulphide in water after its conversion into $CS_2N_3^-$ by reaction with excess of azide.[12]

Effect of foreign ions in neutral solution. The stock solution of sodium 1,2,3,4-thiatriazol-5-thiolate undergoes slow decomposition[1] on standing, according to the equation:

$$CS_2N_3^- \rightarrow SCN^- + S + N_2$$

Thiocyanate or azide in 200-fold ratio does not interfere in the spectrophotometric determination. The $CS_2N_3^-$ concentration during the decomposition of the solution can be determined after extraction of the sulphur suspension with carbon disulphide.[10] The solvent absorbs at 313 nm but is easily removed by bubbling nitrogen through the solution.

The pseudo-halogen $(CS_2N_3)_2$ is unstable[19] and its spectrum resembles that of $CS_2N_3^-$. Its molar absorptivity at 313 nm is about half that for $CS_2N_3^-$, but between twice and five times that of the $CS_2N_3^-$ ion at 240 and 272 nm respectively.

$(CS_2N_3)_2$ reacts quantitatively with azide, yielding $CS_2N_3^-$ and nitrogen.[4,5] Since azide does not interfere at wavelengths longer than 260 nm, measurements of the absorbance of the sample at 272 and 313 nm, in the presence and absence of N_3^-, make it possible to detect and to estimate the concentration of the di(1,2,3,4-thiatriazol-5-yl) disulphide in solutions of $CS_2N_3^-$.

Polarographic measurement of the anodic mercury dissolution wave provides an alternative way to distinguish and measure the concentration of both $(CS_2N_3)_2$ and $CS_2N_3^-$, because the presence of

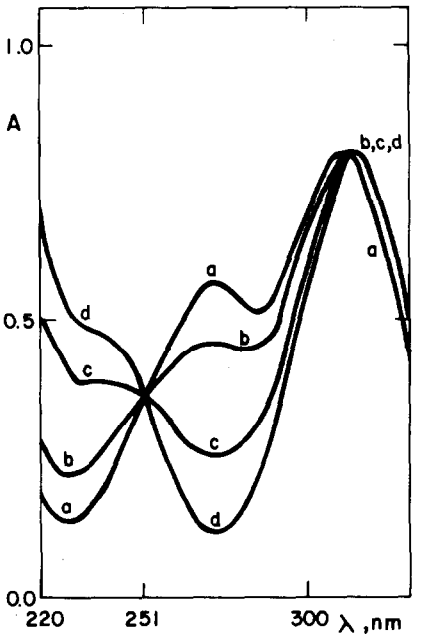


Fig. 2. Ultraviolet spectra of 1.1×10^4M aqueous solutions of $NaCS_2N_3$ at several hydrogen-ion concentrations: (a) 1.0M; (b) 0.10M; (c) 0.010M; (d) 0.0010M; ionic strength 1.00M ($NaClO_4$ + $HClO_4$).

Table 2. Absorbance data for $1.72 \times 10^{-4}M$ $NaCS_2N_3$ at several hydrogen-ion concentrations; $\mu = 1.00M$ ($NaClO_4$), $\lambda = 272$ nm

pH*	A	pH*	A	pH*	A
0.15	0.821	1.20	0.625	1.95	0.354
0.36	0.818	1.35	0.573	2.22	0.270
0.75	0.763	1.48	0.514	2.70	0.216
0.95	0.708	1.72	0.419	2.96	0.204
3.37	0.190	3.80	0.190		

* Expressed in terms of the hydrogen-ion concentration calculated from the perchloric acid added.

$(CS_2N_3)_2$ in $CS_2N_3^-$ solutions introduces a cathodic component in the anodic wave for $CS_2N_3^-$.

NO_3^- and NO_2^- interfere if their respective concentrations are 8 and 15 times that of $CS_2N_3^-$.

The following ions do not interfere when present in concentration 100 times that of $CS_2N_3^-$: CNO^-, CN^-, Cl^-, Br^-, I^-, IO_4^-, $S_2O_3^{2-}$, S^{2-}, CO_3^{2-}, HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, ClO_4^-, ClO_3^-, IO_3^-.

Aluminium, alkali and alkaline earth metal ions do not interfere.

Effect of pH. It was found that the $CS_2N_3^-$ spectrum remains unchanged over the pH range 3–12. In acidic solutions the decomposition of the ion is markedly increased.[10] At pH lower than 3, it begins to be protonated to produce HCS_2N_3, a fairly strong acid.[20] Figure 2 shows the change in the spectrum with increase in acidity, expressed in formal pH values; the pure acid form exhibits a maximum at 310 nm with molar absorptivity of 7.0×10^3 $l.mole^{-1}.cm^{-1}$ and another maximum at 272 nm, with molar absorptivity of 5.3×10^3 $l.mole^{-1}.cm^{-1}$. There is an isosbestic point at 251 nm. From measurements at 272 nm (Table 2) it is possible to calculate the ionization constant of HCS_2N_3 by using the equation:[21]

$$pK = pH + \log\left(\frac{A_0 - A_{CS_2N_3^-}}{A_{HCS_2N_3} - A_0}\right)$$

where A_0 is the absorbance at 272 nm for the mixture of the two forms at a particular pH (referred to hydrogen-ion concentration and not activity) and $A_{CS_2N_3^-}$ and $A_{HCS_2N_3}$ are the absorbances of the essentially basic and acid forms, respectively. A value of $(3.1 \pm 0.1) \times 10^{-2}$ mole/l. was obtained for the stoichiometric ionization constant at 25° and ionic strength 1.0*M* (sodium perchlorate). This value differs to some extent from those obtained at low ionic strength at 25°, by Browne[20] and Hantzsch:[23] 2.4×10^{-2} and 2.14×10^{-2} mole/l. respectively.

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SYNTHESIS OF CERTAIN PYRIDINYL AND DIAZINYL HYDRAZONES CONTAINING ONE OR MORE FERROIN GROUPS, AND THEIR CHROMOGENIC REACTIONS WITH IRON, COPPER, COBALT AND NICKEL

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Summary—Fifteen new hydrazones with one or more ferroin groups were prepared, and their chelation and chromogenic properties with iron(II), copper(I), cobalt(II) and nickel(II) were investigated. Improved sensitivity in the spectrophotometric determination of cobalt, copper, and nickel is provided by several of the new compounds. Several others are capable of forming unusually stable and interesting binuclear iron(II) complexes.

Hydrazones with ferroin groups generally afford high sensitivity as chromogenic reagents for nickel and cobalt as well as for iron and copper ions.[1–6] Two outstanding examples are pyridine-2-carboxaldehyde-2-quinolylhydrazone[7–9] and 2-benzoylpyridine-2-pyridylhydrazone.[10,11] Compounds of this type have not been extensively explored. We have undertaken a search for more sensitive or selective reagents from amongst them.

A previous communication described the chromogenic properties of some mono- and bishydrazones of benzil and 2,2′-pyridil.[12] Here we report the synthesis and metallochromic properties of the 2-pyridinyl and pyrazinyl hydrazones of a number of diazinyl and 2-pyridinylmethyl ketones and some substituted glyoxal monoximes. Preparation of the ketones was described earlier together with results of a study of their oximes as ferroin-type reagents.[13]

In addition to their chromogenic properties, several of the compounds to be described are of special interest in that they possess two ferroin chelation sites that could be utilized in chelating two metal ions simultaneously, giving rise thereby to polynuclear complexes.

EXPERIMENTAL

Reagents

Preparation of hydrazones (I)–(XV). A mixture of 0.005 mole each of ketone or ketone oxime and substituted hydrazine dissolved in 25 ml of absolute ethanol was heated under reflux for 3 hr. After evaporation of the ethanol, the resulting hydrazone was recrystallized from the solvent indicated in Table 1 or 2.

Reagent solutions (0.01 *M*). Weighed amounts of the compounds to be tested were dissolved in appropriate volumes of ethanol.

Standard solutions of metal ions. Weighed quantities of pure metal were dissolved in a slight excess of either hydrochloric or nitric acid and diluted to a measured total weight with distilled water.

Buffer solutions and iron-free hydroxylamine hydrochloride solution were prepared as described previously.[14]

Chelation studies

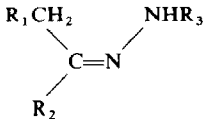
The pH range over which colour formation occurred, wavelengths of maximum absorbance, molar absorptivities, and conformance to Beer's law were determined for each metal ion and test compound combination. Procedures are described elsewhere.[14] Ligand:metal ratios for the iron(II) chelates were determined by the mole-ratio method.[15]

RESULTS AND DISCUSSION

Except for minor differences the chromogenic reactions of compounds (I)–(XV) with the metal ions tested occurred over the pH range 2–11. Maximum colour development resulted between approximately pH 5 and 11. Colours of the iron(II) chelates proved pH-dependent, with colour changes occurring in the region of pH 5–6. Such behaviour undoubtedly accompanies ionization of the hydrogen atom of the hydrazone group.

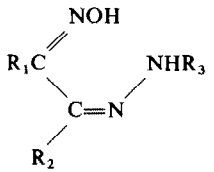
The newly synthesized compounds formed copper, cobalt, and nickel chelates having very high molar absorptivities as evidenced by the spectral data compiled in Tables 3 and 4. None, however, is particularly outstanding as an iron chromogen in comparison with other ferroin-type chromogens. Several exhibit molar absorptivities for cobalt or nickel that are higher than any previously reported compounds of the ferroin or hydrazone types. Thus, compound (V) should prove a more sensitive chromogenic reagent

Table 1. Substituted hydrazones of 2-pyridinyl- or diazinyl-methyl ketones



	R_1	R_2	R_3	m.p. °C	Crystallization Solvent	Formula	Analysis Calcd., % C	H	N	Found, % C	H	N
I	2-C_5H_4N	2-C_5H_4N	Pyrazinyl	164	CH_3OH	$C_{16}H_{14}N_6$	66.19	4.86	28.95	65.9	4.9	28.9
II	2-C_5H_4N	Pyrazinyl	2-C_5H_4N	122	CH_3OH-H_2O	$C_{16}H_{14}N_6$	66.19	4.86	28.95	66.2	4.8	29.0
III	2-C_5H_4N	Pyrazinyl	Pyrazinyl	179	CH_3OH	$C_{15}H_{13}N_7$	61.85	4.49	33.66	61.6	4.6	33.3
IV	2-C_5H_4N	4-Pyrimidinyl	2-C_5H_4N	149	CH_3OH	$C_{16}H_{14}N_6$	66.19	4.86	28.95	65.9	4.9	29.0
V	2-C_5H_4N	4-Pyrimidinyl	Pyrazinyl	187	CH_3OH	$C_{15}H_{13}N_7$	61.85	4.49	33.66	61.8	4.5	33.4
VI	Pyrazinyl	2-C_5H_4N	2-C_5H_4N	154	CH_3OH	$C_{16}H_{14}N_6$	66.95	4.86	28.95	66.2	4.8	29.1
VII	Pyrazinyl	2-C_5H_4N	Pyrazinyl	195	C_2H_5OH	$C_{15}H_{13}N_7$	61.85	4.49	33.66	61.5	4.6	33.8
VIII	Pyrazinyl	Pyrazinyl	2-C_5H_4N	139	CH_3OH	$C_{15}H_{13}N_7$	61.85	4.49	33.66	61.6	4.5	33.3
IX	Pyrazinyl	Pyrazinyl	Pyrazinyl	216	C_2H_5OH	$C_{14}H_{12}N_8$	57.53	4.14	38.33	57.3	4.2	37.8
X	4-Pyrimidinyl	2-C_5H_4N	2-C_5H_4N	128	CH_3OH	$C_{16}H_{14}N_6$	66.19	4.86	28.95	65.9	4.9	28.8
XI	4-Pyrimidinyl	2-C_5H_4N	Pyrazinyl	163	CH_3OH	$C_{15}H_{13}N_7$	61.85	4.49	33.66	61.5	4.5	33.7

Table 2. Hydrazones of substituted glyoxal monoximes



	R_1	R_2	R_3	m.p. °C	Crystallization Solvent	Formula	Analysis Calcd., % C	H	N	Found, % C	H	N
XII	2-C_5H_4N	2-C_5H_4N	2-C_5H_4N	237	C_2H_5OH	$C_{17}H_{14}N_6O$	64.14	4.43	26.40	64.2	4.4	26.6
XIII	2-C_5H_4N	2-C_5H_4N	C_6H_5	213	C_2H_5OH	$C_{18}H_{15}N_5O$	68.13	4.76	22.07	68.1	4.8	22.1
XIV	2-Pyrazinyl	2-C_5H_4N	2-C_5H_4N	258	C_2H_5OH	$C_{16}H_{13}N_7O$	60.21	4.10	30.71	59.9	4.2	30.3
XV	4-Pyramidinyl	2-C_5H_4N	2-C_5H_4N	237	C_2H_5OH	$C_{16}H_{13}N_7O$	60.21	4.10	30.71	60.0	4.3	30.5

Table 3. Absorption properties of iron(II) chelates as a function of pH

Ligand	pH 4.0 Colour	λ,nm	ϵ, 10^3 $l.mole^{-1}.cm^{-1}$	pH 7.0 Colour	λ,nm	ϵ, 10^3 $l.mole^{-1}.cm^{-1}$
I	Orange-brown	563	6.5	Green	603	7.7
		530	5.9			
II	Red-brown	553	7.0	Yellow-green	592	6.2
		477	6.8			
III	Yellow-green	615	4.7	Yellow-green	621	5.3
IV	Green-brown	598	6.9	Green	615	8.0
		569	7.0		460	25.0[a]
V	Yellow-green	629	8.3	Yellow-green	633	8.9
		481	20.4[a]		491	18.0[a]
VI	Orange	529	10.0	Orange	529	9.2
VII	Orange-brown	565	6.7	Brown-green	596	6.7
VIII	Red	551	7.9	Green	593	6.7
		473	7.5			
IX	Yellow-green	620	5.1	Yellow-green	620	5.6
X	Orange	528	10.2	Orange	528	8.5
		469	7.7			
XI	Orange-brown	561	6.7	Brown-green	594	6.8
		529	6.2			
XII	Red-brown	529	9.03	Green	568	8.3
		454	8.02		452	16.0[a]
XIII	Orange	530	10.8[b]	Red	539	9.8[b]
XIV	Red-brown	565	7.2	Green	568	8.3
		530	7.7		448	18.0[a]
		453	14.0[a]			
XV	Red-brown	566	7.2	Green	569	8.7
		531	7.5		451	18.6[a]
		451	14.4[a]			

[a] Blank also absorbs appreciably at this wavelength.
[b] Beer's law not followed unless a large excess of ligand is present.

for nickel and (IV) for cobalt than any ferroin-type compounds yet described.

Examination of the spectra of the metal chelates of any given compound of the group studied reveals that simultaneous determinations of all four metals (iron, copper, cobalt, and nickel) would be impractical because of close, overlapping absorption bands of at least two of the four metals. However, many possibilities are evident for simultaneous determinations to be made of two or even three of these metal ions in the absence of the others. For example, compound (V) should prove satisfactory for the simultaneous

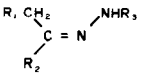
Table 4. Absorption properties of copper, cobalt, and nickel chelates[a]

Ligand	Copper(I) Colour[b]	λ,nm	ϵ, 10^3 $l.mole^{-1}.cm^{-1}$	Cobalt(II) Colour[b]	λ,nm	ϵ, 10^3 $l.mole^{-1}.cm^{-1}$	Nickel(II) Colour[b]	λ,nm	ϵ, 10^3 $l.mole^{-1}.cm^{-1}$
I	O	483	18.9	O	499	26.0	Y	470	39.0
II	R	517	15.4	M	533	22.0	OR	501	30.0
III	R	514	17.0	M	533	23.3	OR	501	36.5
IV	O	497	27.0	R	509	36.0	Go	480	52.0
V	O	498	32.0[c]	R	516	30.1	O	492	55.0
VI	Y	465	16.5[c]	Go	482	31.0	Go	454	30.4[c]
VII	Y	478	19.0	O	492	25.1	Go	466	46.0[c]
VIII	R	516	15.5	M	530	23.4	O	500	33.0
IX	R	521	13.0	M	538	24.0	O	499	36.6
X	Y	468	17.6	O	482	27.9	Y	456	18.0
XI	Go	476	21.0[c]	O	500	23.8	Y	469	40.0
XII	Y	470	21.4	O	482	27.4	Y	460	18.0
XIII	Y	d	d	Y	d	d	Y	d	d
XIV	Y	470	24.0	O	483	33.7	Y	455	24.6
XV	Y	470	25.5	O	481	35.0	Y	460	23.0

[a] Measured in the visible region for ethanol–water solutions buffered at pH 7 with ammonium acetate.
[b] Colour key: Br = brown, Go = Gold, Gr = green, M = magenta, O = orange, R = red, and Y = yellow.
[c] Beer's law not followed unless a large excess of chromogen is present.
[d] Spectra of metal chelate and of free ligand are very nearly the same.

determination of iron, cobalt, and nickel in the absence of copper. Likewise, compound (V) should be effective for the simultaneous determination of either cobalt and nickel or iron and copper.

Compounds (I)–(XI) can exist as *syn* or *anti* stereoisomers. Either form can act as a bidentate chelating agent; however, only the *anti* isomer is capable of terdentate chelation. Our mole-ratio studies indicate that at pH 4 or 7 all eleven compounds form iron(II) chelates with ligand:iron ratios of 2.0–2.2. Thus all exist predominantly in the *anti*-isomer form, shown below:

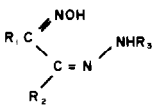


The presence of some *syn*-isomer in the synthesized products is indicated by the fact that mole-ratio values slightly in excess of 2.0 were obtained. Very little curvature was evident in the mole-ratio plots, except in the immediate vicinity of the value 2.0, indicating that the iron(II) chelates are strong and quantitatively formed.

Compound (XIII) has a phenyl group in place of a pyridyl group, which should prevent it from acting as a terdentate ligand. The 3:1 ligand:iron(II) ratio found in the mole-ratio studies confirms this. In fact the bidentate action of (XIII) towards hexacovalent iron(II) appears to take place at the oxime ferroin group rather than the hydrazone moiety. Structural models indicate that the phenyl group can give rise to steric hindrance in chelation of iron by more than one ligand if the aza-nitrogen of the hydrazone group is utilized in co-ordination.

Furthermore, it was found that there was considerable curvature in the mole-ratio plots for (XIII) and iron(II), especially at lower pH. This is consistent with the weak co-ordination expected for oxime nitrogen atoms.[13,16]

Compounds (XII)–(XV) can also exist as *syn* or *anti* isomers, but with greater complexities because both the oxime and the hydrazone moiety can have the *anti* or *syn* configuration. The results for (XII), (XIV) and (XV) suggest that the *anti* configurations (shown below) predominate in each case. A more interesting



and certainly significant observation, however, is that mole-ratio values of 1.4–1.6 were obtained for (XII), (XIV) and (XV) at pH 7. Such values clearly indicate that these compounds are capable of simultaneously utilizing the terdentate function of the R_2, R_3 and hydrazone grouping and the bidentate ferroin function of the R_1 and oxime group. Such a phenomenon can only occur if separate iron(II) ions are chelated by the two different portions or regions of the same ligand. To satisfy this requirement as well as the octahedral co-ordination preferred by iron(II), we therefore propose the following model. Iron(II) ions are first complexed by ligands (XII), (XIV) or (XV) acting as terdentate ligands to form $FeL_2^{(2-2n)+}$, which at pH 7 may be uncharged or negatively charged depending on the extent of ionization of the hydrazone and oxime hydrogen atoms. Additional iron(II) ions can then be chelated by the FeL_2 species, each utilizing one of two available bidentate ferroin groups to form $[Fe(FeL_2)_3]^{(4-6n)+}$, where n is the number of ionized hydrazone and oxime hydrogen atoms per ligand. The ligand:metal ion ratio for this binuclear complex is 6:4, the same as that found for (XII), (XIV) and (XV) within experimental error.

Table 5. Mole-ratio of iron(II) chelates as a function of pH

Ligand	Ligand/iron mole-ratio pH 4	pH 7
XII	2.22	1.49
XIII	3[a]	3[a]
XIV	2.29[b]	1.61
XV	2.25	1.44

[a] Very weak complex required use of matching technique.[15]

[b] Same numerical result obtained by varying ligand concentration as when metal ion concentration was varied while the other reactant concentration was held constant.

Clearly a neutral or negatively charged $FeL_2^{(2-2n)+}$ species should co-ordinate more readily than a positively charged species to a positively charged iron(II) ion. Decreasing the pH of the solution would be expected to discourage ionization of hydrogen atoms, thereby increasing the positive charge on $FeL_2^{(2-2n)+}$ species and discouraging formation of $[Fe(FeL_2)]^{(4-6n)+}$ species. This was confirmed by experiment. At pH 4 iron(II) chelates with ligand:metal ratios in the range 2.2–2.3 were found for (XII), (XIV) and (XV). Mole-ratio values greater than 2 are believed to result from the presence of some *syn*-isomer which can only act in a bidentate mode to give a mole-ratio value of 3.

Further investigations are necessary to elucidate more fully the identity and structure of the binuclear complexes formed by (XII), (XIV) and (XV). Isolation and X-ray diffraction studies of their various metal chelates should prove most enlightening.

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DETERMINATION OF PENICILLINS BY DESULPHURIZATION WITH LEAD AND EDTA TITRATION

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Summary—A new, simple, accurate and rapid method is described for the determination of total penicillins in pharmaceutical preparations. The method is based on desulphurization with potassium plumbite whereby one mole of lead sulphide is formed per mole of penicillin. The excess of lead ions is titrated with EDTA at pH 4.5, with use of the lead ion-selective electrode. Results are reproducible within ±0.5% and compare favourably with those obtained by the procedures of the United States and British Pharmacopoeias.

Methods have been described for the analysis of penicillins based on spectrophotometric, fluorimetric, titrimetric, gravimetric and chromatographic procedures.[1,2] The spectrophotometric methods are mainly based on the reaction of the β-lactam ring with a suitable condensing agent to form chromogens.[3–5] The infrared absorption of the β-lactam carbonyl group at 1760 cm^{-1} may also be used for the assay.[6] Some of these methods suffer from the disadvantages of poor selectivity, insufficient accuracy, and a time-consuming extraction step implicit in most of the procedures.

Bromometric analysis of penicillins[2,7,8] suffers from lack of stoichiometry due to nuclear bromination of the aromatic moiety of the substituent groups; *e.g.*, while the penicillin G molecule consumes 7 atoms of bromine, that of penicillin O apparently consumes 15.6 atoms.[2] The iodometric method, which is the method of assay of general applicability at the present time and the one recommended by both the British and United States Pharmacopoeias[9,10] for the determination of total penicillins, also suffers from lack of stoichiometry, which fluctuates between 8 and 9 equivalents of iodine per mole.[2] The concentration of the iodide ion in the iodine reagent, and the pH of the solution both significantly affect the stoichiometry of the reaction, which necessitates the determination of the exact equivalence by analysing a pure standard sample under the same experimental conditions.[9]

Methods based on the reaction with metal ions have been reported. Penicillin G has been determined by extraction into nitrobenzene as an ion-pair complex with tris(1,10-phenanthroline)–cadmium, followed by measurement of the cadmium in the nitrobenzene phase by atomic-absorption spectrometry.[11] Reaction with copper(II) followed by titration of the excess of copper with EDTA has been suggested.[12] Titration of penicillins with mercury(II), after alkaline or enzymatic hydrolysis, has also been suggested, the iodide ion-selective electrode being used.[13] These methods are not of general applicability and are adversely affected by the appreciable solubility of the metal–penicillin complexes.

Recently, a penicillin-sensitive electrode has been developed in which the enzyme penicillinase is immobilized in a thin membrane of polyacrylamide gel moulded around, and in intimate contact with, a glass electrode.[14] The increase in hydrogen-ion concentration due to the formation of penicilloic acid is sensed by the glass electrode and the potential response is recorded. However, several disadvantages militate against the effective use of this electrode in quantitative analysis. These are the non-Nernstian response of the electrode, the partial precipitation of some penicillins at the pH required for the optimum enzyme activity, and the accumulation of part of the test sample in the membrane.

The present investigation was undertaken with the aim of developing a new, simple, rapid and accurate method, free from many of the defects usually encountered in other methods, for the analysis of total penicillins. The reaction of an alkaline plumbite solution with penicillins has been investigated in order to optimize the conditions required for their stoichiometric degradation to lead sulphide, followed by subsequent measurement of the excess of lead ions with the lead ion-selective electrode.

EXPERIMENTAL

Reagents

All the reagents used were analytical-reagent grade, and doubly distilled water was used throughout. Solutions of 0.005*M* EDTA, 0.02*M* potassium plumbite (prepared by dissolving 6.624 g of lead nitrate in 1 litre of 0.2*M* potassium hydroxide) and acetate buffer of around pH 4.5 (prepared by mixing equal volumes of 1*M* acetic acid and 1*M* sodium acetate) were used.

Apparatus

A Radiometer PHM 22r pH-meter and an Orion lead ion-selective electrode (Model 94-82) were used in conjunction with an Orion double-junction reference electrode

(Model 90-02), with 10% potassium nitrate solution in the outer compartment. The data were plotted on Gran-plot paper, with 10% volume correction (Orion part no. 90-00-90).

Procedure

Weigh out accurately 10–25 mg of the finely powdered penicillin sample, and carefully transfer to the bottom of a Pyrex test-tube (10 × 1 cm). Add 3 pellets of potassium hydroxide (~0.2–0.3 g) and place the tube in a sand-bath at 250–300° for 5–8 min. Cool to room temperature, add 5 ml of 0.02*M* potassium plumbite, shake, and place in a boiling water-bath for 2 min. Transfer the contents quantitatively into a 250-ml beaker, wash the tube out with portions of pH-4.5 acetate buffer solution, and make up to 50 ml with the buffer solution. Place the lead electrode and the double-junction reference electrode in the solution. While stirring, make from three to five 1-ml additions of 0.005*M* EDTA and after each addition record the potential when it attains a constant value (after *ca.* 20 sec). Plot the results on Gran-plot paper and draw a straight line through the points to obtain the intercept on the horizontal axis, which indicates the equivalence-point volume. Carry out a blank experiment.

For formulated penicillins, grind up 20 tablets, or mix the contents of 5 vials or capsules. Weigh out an amount of the powder equivalent to 20–30 mg of the penicillins, transfer it into a test-tube, and follow the procedure.

Calculate the content of penicillin according to the equation:

$$\text{Total penicillin (mg)} = M(V - v + f) \times \text{MW}$$

where M is the molarity of the EDTA solution, V and v are the volumes (ml) of EDTA consumed in the blank and experiment, respectively, f is a correction factor (equivalent to 0.4 ml of 0.005*M* EDTA) due to the solubility of lead sulphide in 50 ml of the buffer solution, and MW is the molecular weight of the penicillin.

RESULTS AND DISCUSSION

Reaction of penicillins with alkali metal plumbite

The thiazole nucleus is known to break down rapidly on treatment with dilute alkali, liberating sulphide ions. The reaction is enhanced by the presence of the plumbite ion which precipitates as lead sulphide.[15] However, penicillins which contain a thiazolidine ring react with dilute alkali to give organo-sulphur degradation products.[16] Attempts to react benzylpenicillin with 0.2*M* plumbite solution, and to measure the free lead concentration after various time intervals with the lead ion-selective electrode, revealed that penicillins resist desulphurization to sulphide even when boiled for up to 2 hr.

Reaction with potassium hydroxide solutions of various concentrations followed by addition of lead ions showed that with 60% potassium hydroxide solution, the maximum attainable concentration at room temperature, only 25% of the penicillin's thiazolidine sulphur is liberated in the form of lead sulphide. Reaction with solid potassium hydroxide was tried next. This salt melts in its water of hydration at 80° to give an 85% solution. The concentration of this solution increases with increase in temperature up to the dehydration point at 143°.[17] Potassium hydroxide is the alkali of choice as it has the advantage over sodium hydroxide that potassium sulphide is more stable than sodium sulphide at higher temperatures.[17]

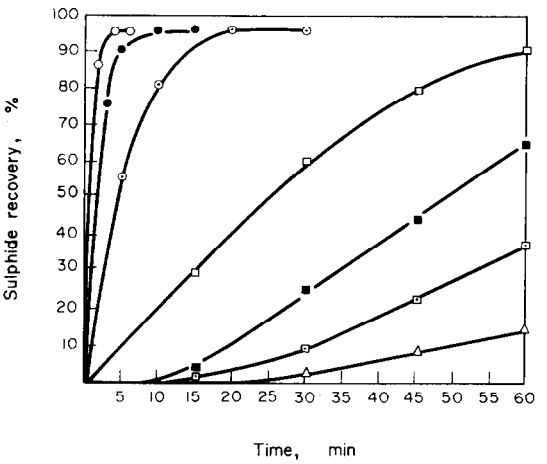

Fig. 1. Effect of temperature on the desulphurization of benzylpenicillin by reaction with solid potassium hydroxide and plumbite: Reaction with potassium hydroxide at: ○, 280°; ●, 250°; ⊙, 200°, □, 175°; ■, 150°, ⊡, 125° and △, 100°.

The effect of temperature on the decomposition of benzylpenicillin with solid potassium hydroxide followed by digestion with potassium plumbite, (with sulphide as the product) is shown in Fig. 1. At 250–280°, the reaction is fast enough to ensure quantitative formation of one mole of lead sulphide per mole of penicillin within only 5 min. This was demonstrated by: (*i*) gravimetric measurement of the precipitate, confirming the stoichiometric formation of one mole of lead sulphide per mole of penicillin; (*ii*) the absence in the infrared spectrum of the lead sulphide precipitate of any absorption bands typical of organic compounds; and (*iii*) the absence of sulphur in the organic extract of the reaction products. The time needed for decomposition at various temperatures is shown in Table 1.

Nature of the reaction products

The reaction was investigated by identifying the decomposition products of benzylpenicillin. The reaction was carried out in a test-tube with side-arm attached to the gas-sampling unit of a Beckman gas–liquid chromatograph (Model G.C-M). The volatile products were swept in a stream of helium into a Chromosorb W–20% dioctyl sebacate column maintained at 120°. The thermal-conductivity detector, operated at 350 μA, gave only one peak, with retention time corresponding to that of ammonia. The reaction residue was acidified with hydrochloric acid to pH 2, extracted with ether, which was then evaporated, and found to yield phenylacetic acid as confirmed by elemental analysis, infrared spectrum and mixed melting point comparison with an authentic specimen. Carbon dioxide was also detected during the acidification. Thus, four breakdown products were identified: potassium sulphide, ammonia, carbon dioxide and phenylacetic acid.

Table 1. The time required for quantitative decomposition of benzylpenicillin to yield sulphide by reaction with solid potassium hydroxide and plumbite

Temperature, °C	Time
80	2 days*
100	8 hr*
150	4 hr*
175	70 min*
200	17 min
250	7 min
280	4 min

* Nitrogen gas was used for flushing throughout the reaction time to avoid slow aerial oxidation of sulphide.

Measurement of the free lead concentration with the lead ion-selective electrode

The use of lead in this reaction is necessary not only to precipitate the sulphide ions but also to ensure complete degradation of the penicillin-sulphur. This was substantiated by direct measurement of the sulphide ions, after reaction with alkali, with the sulphide ion-selective electrode and by silver nitrate titration with use of the same electrode, when incomplete desulphurization was revealed. The catalytic effect of lead ions on the decomposition of many sulphur compounds to sulphide ions has been previously reported.[15,18] The indirect determination of the sulphide ions by measurement of the excess of lead ions seemed to be the logical final step in the procedure.

The pH of the reaction solution was adjusted to 4.5 with the acetate buffer and the free lead was determined by a potentiometric EDTA titration using the lead ion-selective electrode. The titration procedure was greatly simplified and the precision improved by the use of Gran plots;[19] three additions of titrant were sufficient for locating the equivalence point in the titration. The electrode exhibited a fast response to changes in free lead concentration,[20] but the slight solubility of lead sulphide in the acetate buffer, though not necessitating filtration prior to titration, did require the introduction of a correction factor. This factor was found experimentally to amount to 2 μmole of EDTA per 50 ml of the acetate buffer solution.

The determination of the excess of lead was also attempted, for comparison, by atomic-absorption spectrophotometry. The solution was treated with EDTA to prevent formation of basic lead carbonate, filtered, and diluted 100 times with dilute nitric acid to bring the final lead concentration within the linear range of the calibration curve (1–10 ppm). The solution was then aspirated into an acetylene–air flame and the absorbance of the lead was measured at 217 nm on a Unicam SP 1900 atomic-absorption spectrophotometer. The difference between the total amount of lead added and that remaining after reaction with the penicillins was calculated by using a standard curve prepared under similar conditions with the same background. Although the results obtained by this method were within 1.5% of those obtained by the electrode method, the latter is easier and less time-consuming.

Analysis of pure penicillins

Some pure penicillin samples, containing down to 20 μmole were analysed by the procedure described here and the results were compared with those obtained by applying the standard iodometric procedure of the British Pharmacopoeia.[10] The results obtained by the two methods agreed within ±0.5% (Table 2). These figures were further compared with the values for elemental analysis for sulphur by combustion in the oxygen flask and titration of the resulting sulphate with barium perchlorate (Thorin indicator).[21] The results by the proposed method and those by the elemental sulphur method agreed within ±0.3%. Repeated determinations by the proposed method on 50 different weights of pure benzylpenicillin showed a relative standard deviation of 0.5%.

Another approach to the analysis of penicillins was also attempted, in which the reactions between penicillins and standard solutions of lead(II), cadmium(II),

Table 2. Determination of some pure penicillins by the proposed method and the iodometric method of the British Pharmacopoeia[10]

	B.P. method			Proposed method		
Sample	Taken, *mg*	Found, *mg*	Recovery, %	Taken, *mg*	Found, *mg*	Recovery, %
Benzylpenicillin, potassium	10.00	9.74	97.4	22.40	21.70	96.9
	17.50	17.01	97.2	13.00	12.64	97.2
Phenoxymethylpenicillin	9.00	8.78	97.6	9.12	8.96	98.2
	15.20	14.78	97.8	9.18	8.96	97.6
Ampicillin, anhydrous	10.00	9.69	96.9	14.87	14.33	96.4
	13.30	12.94	97.3	15.75	15.18	96.4
Benzathin penicillin G	12.00	11.74	97.8	14.84	14.47	97.5
	17.12	16.69	97.5	19.95	19.17	96.1
Procaine penicillin G	19.90	19.54	98.2	14.92	14.67	98.3
	15.65	15.32	97.9	12.50	12.25	98.0

Table 3. Solubility of some metal–penicillin complexes

Sample	Solubility, *g/l.*			
	Cu-complex	Cd-complex	Hg-complex	Pb-complex
Penicillin G, sodium	0.1650	—	0.0402	0.4931
Benzathin penicillin G	0.2602	0.0562	0.0704	0.0746
Ampicillin	0.3553	0.2810	0.0200	0.2486

copper(II) and mercury(II) were followed by using the lead (Orion 94-82), cadmium (Orion 94-48), copper (Orion 94-29) and iodide (Orion 94-53) ion-selective electrodes, respectively. The results obtained were unsatisfactory, owing either to the solubility of some metal–penicillin complexes, as verified by the solubility measurements (Table 3) or to the instability of some of these complexes. Furthermore, some of the excipients normally present in pharmaceutical preparations also react with these ions. However, in the proposed procedure, such excipients decompose during the reaction step with solid potassium hydroxide.

Determination of total penicillins in some pharmaceutical preparations

In order to assess the applicability of the present procedure for pharmaceutical analysis, the possible interferences from some common excipients and diluents used in the preparation of capsules, suspensions and injections were investigated. Amounts of

Table 4. Effect of some excipients on the determination of benzylpenicillin

Excipient	Weight taken, *mg*		Benzylpenicillin found	
	Excipient	Benzylpenicillin	Weight, *mg*	Recovery, %
Magnesium stearate	5.43	11.82	11.50	97.3
	6.64	10.55	10.24	97.1
Talc powder	5.84	13.14	12.75	97.0
	4.46	15.68	15.30	97.6
Sodium citrate	3.84	10.18	9.91	97.3
	6.72	13.74	13.36	97.2
Polyvinylpyrrolidone	3.34	11.64	11.34	97.4
	5.63	13.03	12.68	97.3
Tween-80	6.81	10.90	10.59	97.2
	6.17	9.87	9.67	98.0
Lactose	5.16	16.43	16.12	98.1
	5.00	10.10	9.84	97.4
Glucose	6.94	10.77	10.45	97.0
	5.18	9.75	9.51	97.5
Carboxymethyl cellulose	6.60	9.19	8.95	97.4
	7.11	9.34	9.07	97.1

Table 5. Determination of total penicillins in some pharmaceutical preparations by the proposed method and the iodometric method of the British Pharmacopoeia[10]

Sample	Source	Labelled active amount	B.P. method Found, *mg*	Proposed method Found, *mg*
Ampicillin	El-Nile Pharm. Co. (Egypt)	250 mg per capsule	258 255	256 252
"Prostaphlin" Oxacillin, sodium	Bristol Lab. N.Y. (U.S.A.)	250 mg per capsule	253 252	256 254
"Ospen" Phenoxymethyl penicillin	El-Nile Pharm. Co. (Egypt)	600 mg per tablet	598 594	592 593
"Dexacillin" Epicillin	Squibb & Sons N.Y. (U.S.A.)	250 mg per capsule*	— —	240 237
Penicillin G, sodium	CID Pharm. Co. (Egypt)	600 mg per vial	583 580	578 580

* No official procedure is available for the analysis of this new product

magnesium stearate, talc, sodium citrate, carboxymethylcellulose, Tween-80, polyvinylpyrrolidone, glucose and lactose far in excess of their normal levels in the pharmaceutical preparations were added to both a reagent blank and pure benzylpenicillin. No effect was noticed from any of these materials (Table 4). It is noteworthy that neither magnesium nor citrate ions have any effect on the accuracy of the procedure. The magnesium–EDTA reaction takes place only at a much higher pH than that used here for the reaction between lead and EDTA, and the citrate ion is decomposed by the alkali during the reaction step.

Penicillins in some pharmaceutical preparations were determined by both the present method and the standard iodometric method of the British and United States Pharmacopoeias.[9,10] The results given in Table 5 show agreement within $\pm 1\%$. The accuracy is quite satisfactory as the permissible recovery limits for the active ingredients, according to both Pharmacopoeias,[9,10] range between 95 and 105%.

The present procedure therefore offers, in addition to satisfactory accuracy, a convenient solution to a number of problems associated with the determination of total penicillins in simple and complex formulations, especially those relating to stoichiometry, simplicity and rapidity. Analysis of a penicillin sample takes less than 15 min whereas the iodometric procedure requires 60 min. The procedure has been used in quality control analysis at El-Nasr Pharmaceutical Chemicals Co. in parallel with the iodometric method, for the past two years.

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AUTOMATED CONTINUOUS-FLOW DETERMINATIONS OF SERUM PROTEINS BY PULSE POLAROGRAPHY

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Summary—A new flow-through cell is described for application of the dropping mercury electrode to the determination of serum proteins in an automated continuous-flow system. By using differential pulse polarography with short controlled drop times, it is possible to run a rapid automated system at sampling rates of up to 120 per hour with approximately ±1% precision and less than 3% carry-over. With the Brdička reagent, hexa-amminecobalt(III) chloride, various serum proteins can be determined in the range 5–50 μg/ml. The method therefore offers a rapid and sensitive automated procedure for determination of serum proteins.

The polarographic determination of serum proteins has been studied extensively,[1–5] particularly in relation to possible applications in cancer research.[2] Previous studies[3] have shown that the combination of pulse polarography with Brdička's hexa-amminecobalt(III) chloride reagent for the determination of serum proteins offers good sensitivity, while a new reagent, an Rh(III)-substituted ethylenediamine complex, has recently been found[4] to give a highly sensitive determination of serum proteins and to be applicable[5] to accurate determination of total serum protein.

The widespread application of polarographic methods in clinical chemistry appears to have been delayed by the lack of reliable automated equipment for the rapid analysis of large numbers of samples. The automation of polarographic methods has been reviewed:[6–8] examples of automated polarographic or voltammetric methods include d.c., a.c., pulse and anodic stripping procedures at both the dropping mercury electrode (DME) and stationary electrodes.

Differential pulse polarography (dpp) with the DME does not seem to have been applied for rapid analysis in a continuous-flow automated system, however. This paper describes a simple flow-through cell for use with dpp and a controlled drop-timer in a continuous-flow system, and its application to the automated analysis of serum proteins by means of the Brdička reagent. Detection limits and characteristics of protein detection and determination by automated dpp are reported. The system offers a sensitive method for automated protein analysis, which is competitive with conventional colorimetric methods in terms of speed of analysis and sensitivity.

EXPERIMENTAL

Reagents and solutions

A 0.1*M* stock solution of hexa-amminecobalt(III) chloride reagent (Merck Schuchardt) was made up in distilled water, and was diluted as required to cover the range from $1 \times 10^{-3}M$ to $6 \times 10^{-3}M$ at a chosen pH value. To study the effect of pH, the concentration of ammonia was varied, while the concentration of ammonium chloride was maintained constant at 1*M* in the Co(III) solution.

Proteins used in this work were bovine albumin (Nutritional Biochemical Corporation, Fraction V), bovine γ-globulin, Fraction II, and bovine glycoprotein, Fraction VI, both from Miles Laboratories, Inc. Stock solutions (1 mg/ml) were prepared in distilled water, and appropriate dilutions were freshly made as required in the range 20–200 μg/ml.

Instrumentation

A Princeton Applied Research Model 174 polarographic analyser equipped with a drop-timer Model 174/70 and a Mace Laboratory recorder FBQ 100 was used for polarographic analysis in the differential pulse or direct current operational modes. The controls were set as follows: current range 500 μA, modulation amplitude 100 mV, drop-time 1 sec, fixed potential −1.39 V, potential scan-rate 5 mV/sec (when required), chart-speed 500 mm/hr.

Polarographic waves were measured with a three-electrode system consisting of a platinum metal electrode, a saturated calomel reference electrode (SCE) and a dropping mercury electrode as the indicator electrode. Electrode characteristics were: $m = 2.67$ mg/sec, $t = 3.2$ sec at a mercury column height of 56.8 cm measured in 1*M* ammonia buffer at −1.39 V. All measurements were made at room temperature.

The DME was inserted in an air-tight flow-through cell shown in Fig. 1. This newly designed cell is quite different from previously reported flow-through cells[9–15] for continuous polarographic monitoring. The platinum auxiliary electrode was situated upstream from the DME, and allowed operation in the differential pulse mode with a three-electrode system and with accurately controlled drop-times. The third electrode, the SCE, was situated downstream from the cell in the waste solution as shown in the schematic flow diagram in Fig. 2.

For automated pumping of reagents through the flow-cell, a Desaga multichannel peristaltic pump, Type No. 131900, was used. Total solution flow-rates through the cell could be varied over the range 1–20 ml/min per channel with this pump by use of a speed controller and pump tubes varying from 1.00 to 3.0 mm in internal diameter.

Procedure

With the flow system shown in Fig. 2, the reagent and

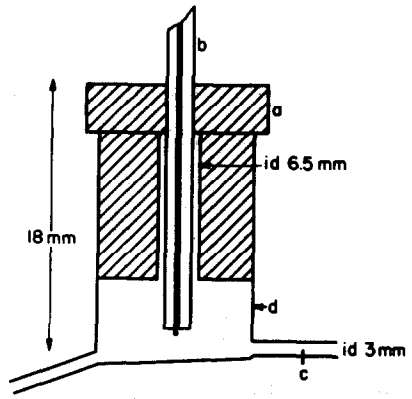

Fig. 1. Flow-through cell constructed of glass. (a) Teflon sleeve; (b) DME; (c) Pt contact; (d) glass cell.

wash solutions were pumped initially through the cell until a constant baseline and a suitable current range, for which the baseline noise was low, were established. In general, unless otherwise stated, a constant flow-rate of 15 ml/min was maintained. For most studies the reagent solution consisted of the complex, $[Co(NH_3)_6]Cl_3$, at a concentration of $6 \times 10^{-3}M$, in $0.4M$ ammonium chloride and $2.0M$ ammonia, while the wash solution was distilled water. Deaeration of the solutions was found to be unnecessary, and air segmentation was used in the flow sytem.

Protein sample solutions were then manually aspirated into the system, followed by a water wash after each sample. The sample-to-wash ratio was kept constant at 1:1 throughout, and sampling and wash times were accurately measured with a stop-watch. The sampling time depended on the hourly sampling rate required, and varied from 30 to 15 sec for sampling rates in the range 60–120 samples per hour.

Current-response to protein concentrations was continuously recorded on the 0.5 or 0.2 mA current ranges, usually with 100 mV amplitude in the dpp mode and a 1 sec controlled drop-time. To study the response to different proteins, calibration curves were constructed for the protein concentration ranges 10–50 μg/ml at a sampling rate of 60 per hour and a solution flow-rate of 15 ml/min. The flow-rate was later varied over the range 5–16 ml/min by using the pump speed regulator.

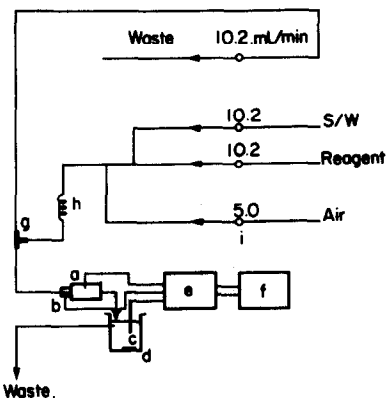

Fig. 2. Schematic diagram of flow system. (a) flow-through cell; (b) Pt auxiliary electrode; (c) SCE; (d) electrolyte solution; (e) PAR model 174; (f) recorder; (g) debubbler; (h) mixing coil; (i) proportioning pump.

RESULTS

The polarographic flow-through cell, and its performance in continuous-flow analysis, were evaluated, and experimental factors which affect the height of the protein catalytic wave, including solution air-segmentation, flow-rate, reagent concentration, pH, surfactants and choice of operational mode and modulation amplitude, were investigated.

Cell construction

The construction of the polarographic flow-through cell was found to be critical for operation in the differential pulse mode. Air-tight fitting of the capillary to the cell with a Teflon sleeve was necessary in order to exclude air bubbles from the cell. Instead of using a mercury-pool as the auxiliary electrode, as suggested by others,[10,14] we used a platinum wire sealed into the cell just upstream from the DME. There was then no problem of accumulation of mercury and run-off from the cell: the mercury drops did not accumulate and were simply flushed out of the cell by the continuously flowing solution. The SCE was positioned downstream from the cell in the stirred waste solution.

In order to choose a suitable value for fixed potential measurements of protein concentrations, we made voltage scans on protein solutions aspirated continuously through the flowing system shown in Fig. 2. A voltage scan for an albumin solution of 50 μg/ml concentration was recorded from −0.8 to −1.8 V. The shape of the polarogram in the continuously flowing solution was similar to that reported previously[1–3] for static solutions. In the differential pulse mode, the Co(II) maximum occurred at −1.18 V and the double protein wave at −1.39 and −1.55 V, corresponding to the A and B protein waves.[3] For polarographic determination of proteins at fixed voltage, the voltage was set at −1.39 V and the current was recorded for different concentrations of protein in the flowing solution.

The hold-up volume within the cell was adjusted by shifting the capillary through the Teflon sleeve. The minimum hold-up volume obtainable with this cell design without causing distortion of the mercury drops was approximately 0.5 ml. As discussed by Blaedel and Strohl[15] small hold-up volumes are preferable if a rapid polarographic response is to be obtained for a flowing stream.

Response times and sampling rates

Rapid response of the detector is essential in continuous-flow analysis. It is preferable that the response to a change in sample concentration should reach 100% of the steady-state signal within the chosen sampling time, but operation is often possible at less than 100% of steady state. Table 1 shows results for the polarographic detector in continuous flow analysis with the solution flow-rate through the cell fixed at a constant value of 15 ml/min. Effects

Table 1. Evaluation of continuous-flow* polarographic detector as a function of sampling rate

Sampling rate *samples/hr*	i_{cat}, μA†	RSD, %§	% of steady state	Carry-over, %
60	297	0.92	98	nil
90	274	1.00	93	0.9
120	253	1.04	90	1.0

* Flow-rate of 15 ml/min through cell.

† Mean catalytic current at −1.39 V for serum albumin at a concentration of 50 μg/ml.

§ Relative standard deviation for 6 replicates of the serum albumin solution.

of changes in solution flow-rate are discussed in a later section.

For a sample solution containing 50 μg of protein per ml, and at a sampling rate of 60 per hour (*i.e.*, 30-sec sampling time followed by a 30-sec wash) the current reached 98% of the steady-state current during the available sampling time. Examples of the continuous-flow read-out are shown in Fig. 3.

At higher sampling rates, the current did not come so close to the steady-state value: some figures are given in Table 1. That the continuous-flow analysis system could be used at this high sampling rate was shown by the results of some tests on the carry-over and precision.

Carry-over and precision

The extent of carry-over from one sample to the next determines the accuracy and precision in continuous-flow analysis systems. As shown in Fig. 3, carry-over was determined by consecutive measurements on samples containing 10, 50 and 10 μg/ml concentrations of albumin. The results given in Table 1 showed carry-over to be negligible at 60 samples per hour and as little as 1% even at 120 samples per hour, indicating acceptable performance of the system at the high sampling rate.

Precision of the continuous-flow system was determined at three sampling rates by replicate measurements on solutions containing 50 μg of albumin per ml. An example of such a series of sample peaks is also given in Fig. 3. A relative precision of 1% is obtainable at the high sampling rate. The system can therefore be operated with satisfactory precision and low carry-over at sampling rates ranging from 60 to 120 per hour.

Calibrations in the dpp and d.c. modes

Calibration curves were constructed for several different proteins, with the continuous-flow system in both dpp and d.c. modes. A comparison of the sensitivities can be made from Fig. 4.

In agreement with the results of dpp studies on static solutions,[3] the dpp calibration curves for albumin, γ-globulin and glycoprotein were linear over the low concentration range studied here. Albumin, however, gave a much greater response than the other proteins, in agreement with other d.c. polarographic studies;[2,7] this is attributed to the different number of disulphide groups in the proteins concerned.

The sensitivity of the dpp method for albumin was almost ten times better than that of d.c. polarography. Furthermore, the d.c. mode was found to be virtually

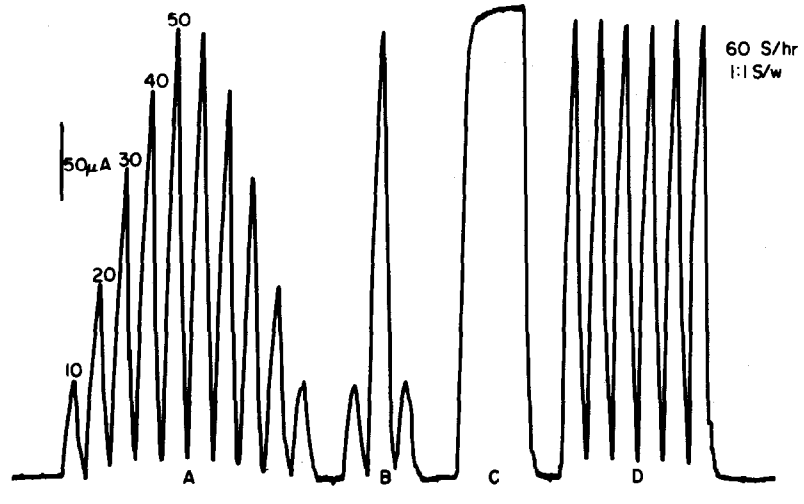

Fig. 3. (A) Calibration for bovine albumin by continuous-flow monitoring of current at a fixed potential of −1.39 V for the concentration range of 10–50 μg/ml at a rate of 60 samples/hr with 1:1 sample-to-wash ratio. (B) Carry-over between sequential samples, 10, 50 and 10 μg/ml, of bovine albumin. (C) Steady-state reading at 50 μg/ml. (D) Replicates of bovine albumin, 50 μg/ml.

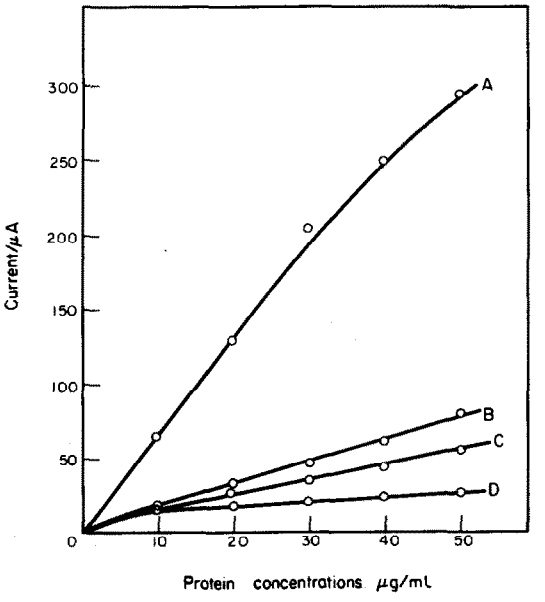

Fig. 4. Calibrations of (A) bovine albumin; (B) bovine γ-globulin and (C) bovine glycoproteins, dpp mode at 60 samples/hr. Co(III) concentration was $6 \times 10^{-3} M$; (D) calibration of bovine albumin, d.c. mode.

useless as a continuous-flow detection method at the low protein concentrations shown in Fig. 4. Because of the current oscillations at the DME, a high noise level was observed both for the continuous baseline read-out and for the sample peaks, and poor peak resolution was obtained even at 60 samples per hour with the d.c. mode. As shown in Fig. 3, dpp operation gave a smooth current read-out for a 1-sec drop-time with adequate sensitivity for protein determinations in the range 5–50 μg/ml.

An added advantage of the dpp mode is the effect of pulse amplitude. The sensitivity for proteins was improved by increasing pulse amplitude, and a linear relationship between sample peak height and amplitude was found over the range 5–100 mV, again in agreement with Paleček *et al.*[3] All calibration measurements for proteins were therefore made with the pulse amplitude set at 100 mV. Under these conditions, extremely high currents were recorded, particularly for albumin, which gave nearly 300 μA for a 50-μg/ml solution.

Effect of flow-rate

Blaedel and Strohl[15] have shown that variations in the rate of flow of solution through a polarographic cell, up to 120 ml/min, have a large effect on the diffusion-controlled steady-state currents at the DME. However, no study of response times at the DME as a function of flow-rate, particularly for operation in the dpp mode, has been reported. We found that the response time for current changes at the DME in the dpp mode showed marked improvement for flow-rates up to about 16 ml/min. Figure 5 shows the relationship between the current peak (as a percentage of the steady-state reading) and total flow-rate through the polarographic cell in the range from about 5 to 30 ml/min. The current readings were taken with a fixed sampling time of 30 sec, and were compared with steady-state current at the same flow-rate. As shown in Fig. 5, there was a marked increase in percentage of steady-state reading up to a flow-rate of about 15 ml/min, at which the current became nearly 100% of the steady-state value. Hence, sampling rates can be markedly improved in an automated polarographic system by use of total flow-rates up to 15 ml/min. The effect will also depend on flow *velocity*, which is controlled by cell geometry and the internal diameter of transmission tubing. However, for the particular cell design described here, 15 ml/min was chosen as the flow-rate giving optimum sampling rates.

Effect of reagents and conditions

In most polarographic determinations, purging of the solutions with nitrogen is necessary in order to eliminate oxygen. In the dpp operational mode, however, we found that purging of reagent solutions and use of nitrogen for bubble segmentation in the flow system was unnecessary at the very negative working potential chosen. At −1.39 V, the contribution from the oxygen reduction wave to the total baseline current was found to be negligible, and hence air segmentation was used in the flow system.

The other important reagent factors controlling the peak height are known[3] to be the Co(III) reagent concentration, the buffer pH and the presence of surfactants in the protein sample solutions.

The effect of varying the Co(III) reagent concentration on the response to albumin is shown in Fig. 6.

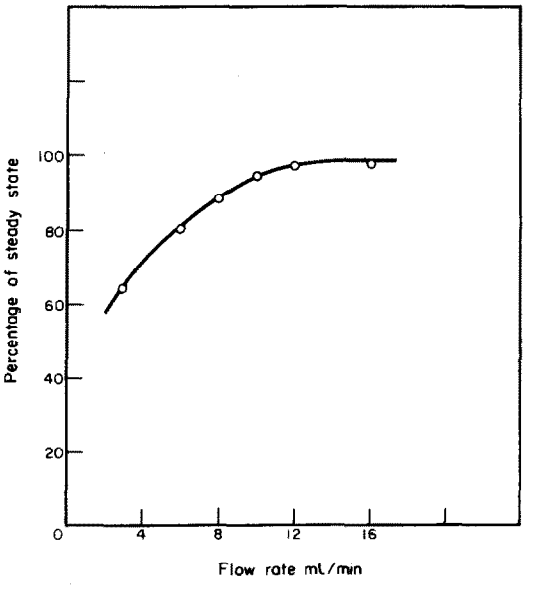

Fig. 5. Effect of flow-rate on response as percentage of steady-state reading at 60 samples/hr.

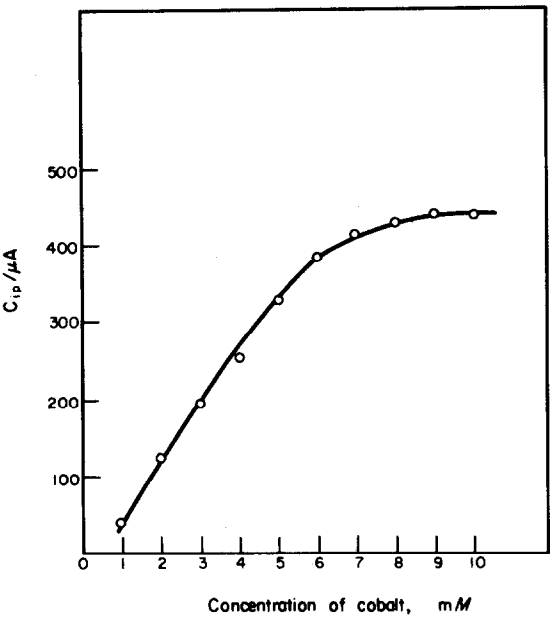

Fig. 6. Effect of cobalt hexamminochloride concentration on the catalytic current of bovine albumin (50 μg/ml).

For routine studies, a concentration of $6 \times 10^{-3}M$ was chosen. At these relatively high Co(III) concentrations, a sharp maximum of the first kind for cobalt was observed at -1.18 V, which decreased as protein concentrations were increased. The cobalt maximum, however, did not appear to interfere with the protein determinations at -1.39 V, and we made no further attempt to eliminate the maximum. Paleček and Pechan[3] recommended using a much lower Co(III) concentration ($6 \times 10^{-4}M$) and small amounts of the surfactant Triton X-100 (2×10^{-5}%) in order to diminish the cobalt maximum, when they determined proteins at concentrations below 1 μg/ml.

Table 2 shows the effect of Triton X-100 on glycoprotein (40 μg/ml) in static solution. In agreement with Paleček and Pechan, we found that Triton X-100 interfered with the protein double wave, causing a marked decrease in wave-height. We therefore did not add Triton X-100 to solutions in our continuous-flow system.

The effect of pH was studied over the range 9.5–10.5 by varying the concentration of ammonia added to a fixed concentration of ammonium chloride (1*M*) in the Co(III) reagent solution. We found that protein response increased linearly with increase in pH, with a slope of approximately 300 μA per pH unit in the dpp mode. The Co(III) reagent solutions were therefore prepared in ammoniacal buffer (1*M*) at pH 10.5 for the investigations described.

Table 2. Effect of surfactant concentration on the Brdička catalytic wave* for glycoprotein

Concentration of Triton X-100, μg/ml	Catalytic current, μA
10	7.3
30	5.4
50	1.6
70	0.2

* Concentration of Co(III) reagent: $1.0 \times 10^{-4}M$.
Concentration of glycoprotein: 40 μg/ml.

DISCUSSION

Previous studies using dpp in flowing systems have been carried out by Cullen *et al.*,[9,10] using the DME as the indicator electrode, by McDonald and Duke[11] using a tubular platinum electrode, and by Alexander and Qureshi[12] at a mercury-pool electrode. However, none of these studies was concerned with output characteristics in a rapidly sampled continuous-flow system. Other polarographic modes have been operated at rates up to 60 samples/hr. The a.c. polarography work of Silvestri[13] made possible the analysis of samples at a rate up to 60 per hour for pharmaceutical applications. Lund and Opheim[14] have operated a d.c. system at 60 samples per hour again for pharmaceutical analysis.

This paper describes a simple cell for dpp which allows the use of the controlled drop-times required for dpp operation. The high sensitivity for the determination of proteins is not surprising, since dpp is well known to discriminate against capacitance current and to give a higher sensitivity than either d.c. or a.c. polarography. This system also responds rapidly to changes in protein concentration, allowing sampling rates of up to 120 samples per hour to be achieved, dependent on total flow-rate past the electrode.

Most of the results were obtained at a fixed solution flow-rate of 15 ml/min through the system, as shown in Fig. 2. However, Blaedel and Strohl[15] have shown that the diffusion current increases with flow-rate for an uncontrolled DME and d.c. polarography. In general, our results agreed with this for the dpp mode. Furthermore, we found that increasing the flow-rates up to about 16 ml/min significantly improved the response of the DME at short controlled drop-times in the dpp modes, as shown in Fig. 6. This allowed us to achieve the high sampling rates mentioned above.

However, there are two problems with the use of high flow-rates, *viz.* high consumption of reagents and unreliable drop formations. The former problem has been critically discussed in recent articles,[16] and obviously the cost and availability of the required reagents for a given system must be a determining factor in design of the flow-manifold. Secondly, faulty drop formation is much more of a problem with the dpp than with the d.c. operational mode. With dpp, the response to a faulty drop is a rapid, negative deviation of baseline with a very slow recovery to the real diffusion current. The slow recovery is a conse-

quence of the slow time-constant of the dpp equipment used, which does not affect d.c. measurement. For reliable operation of the continuous-flow system in the dpp mode, therefore, drop-formation must be exactly reproducible over the period of sampling or information will be lost.

In the application to protein determination, the results obtained for individual proteins compared favourably with those measured manually by others using the same Co(III) hexa-ammine complex as reagent. The response to individual proteins differed appreciably, with albumin giving the most sensitive response of the proteins studied. This agrees with the results of Kalous who, however, used much higher protein concentrations for manual d.c. polarographic measurements. The order of sensitivity for the series of proteins studied was: albumin > γ-globulin > glycoprotein, and linear calibrations were obtained for the concentration range 10–100 μg/ml. In addition, the effects of pH and Co(III) concentration were as expected from results obtained manually. The effect of pulse amplitude also agreed with the manual dpp results of Paleček and Pechan.[3]

The automated dpp method using Brdička's reagent is therefore comparable in sensitivity to other automated methods for protein determination such as the Lowry colorimetric method[18] and the Ag_2S selective electrode method,[19] but similarly suffers from the disadvantage that protein response varies with individual proteins. The automated biuret colorimetric method gives almost equal response with most proteins, and is at present the accepted standard method[20] for determination of total protein in samples such as blood serum. This method, however, lacks sensitivity, and in future it may be possible to develop applications of the continuous-flow polarographic system described here to give both accurate and sensitive determinations of total serum protein, based on the polarographic method recently reported[5] for a catalytic rhodium(III) complex reagent.

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INFLUENCE DE LA COMPLEXATION SUR LE TRANSFERT DES CATIONS EN OSMOSE INVERSE

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Résumé—L'étude de l'influence de la complexation par divers ligands sur le transfert de cations métalliques en osmose inverse a été faite sur membranes de polyamides aromatiques. L'addition de complexant, malgré l'augmentation de volume du soluté diffusant, peut permettre une nette amélioration du transfert des cations métalliques à travers une membrane d'osmose inverse. C'est la solubilité dans la membrane du complexe formé qui est le facteur prépondérant pour l'amélioration du transfert et cette solubilité est liée à la possibilité de former des liaisons hydrogènes entre la membrane et le complexe. Par ailleurs, l'addition de composés solvatant fortement à la fois la membrane et le soluté permet une amélioration du transfert qui augmente fortement avec la pression dans ces conditions. Ces résultats peuvent permettre d'espérer la possibilité de séparation de cations métalliques par complexation spécifique de certains d'entre eux dans un mélange.

L'utilisation de l'osmose inverse pour la récupération de cations métalliques commence actuellement à se développer.[1–11] Cependant, cette technique est concurrencée par des procédés plus souples (échange d'ions, précipitation, etc.) et par des techniques où l'on a la possibilité d'agir chimiquement sur les phénomènes de rétention.

Pour améliorer la méthode et agir chimiquement sur son rendement, on peut penser à l'emploi de complexants organiques plus ou moins spécifiques ou ayant plus ou moins d'affinité avec la membrane. Ainsi, on peut envisager le transfert préférentiel d'un métal complexé par rapport à un autre. Il est donc nécessaire de connaître les mécanismes de transfert pour agir sur eux.

Le mécanisme de transfert des solutés au travers d'une membrane est un sujet controversé. Cependant, la théorie la plus largement acceptée est le mécanisme de flux capillaire–solubilisation préférentielle. Au phénomène physique de porosité s'ajoutent les phénomènes de solubilisation du soluté dans la membrane, puis celle de sa diffusion sous l'effet d'un gradient de pression. Ce mécanisme dépend essentiellement des propriétés physicochimiques de la membrane et des solutés.

Les paramètres les plus importants sont:

—la nature chimique de la membrane: selon l'analyse de Matsuura et Sourirajan[12] pour une membrane donnée, le critère chimique le plus important est "l'effet polaire". La solubilisation du sel dans la membrane dépend de la possibilité de liaisons hydrogène du système soluté–membrane.[13–15]

—les propriétés physico-chimiques de la membrane: la quantité de solvant présent dans la membrane, la façon dont elle lui est liée jouent un rôle important. La perméabilité des membranes plus ou moins hydratées a fait l'objet de nombreuses études.[16–20] La structure, le taux d'hydratation de la membrane et son comportement sont étroitement liés.[18–20] Le gonflement et le rétrécissement de la membrane, s'apparentant à un phénomène de "plasmolyse–turgescence",[21] influent directement sur les coefficients de partage et les constantes de diffusion.

—les propriétés chimiques du sel: le comportement des espèces en solution dépend de la dissociation, de la charge, de la nature et de la dimension des ions associés. Les espèces dissociées sont plus difficiles à solubiliser dans la membrane que celles non dissociées.[22,23] L'augmentation de la charge d'un cation tend à diminuer le coefficient de partage membrane–solvant.[21] Les cations fortement chargés seront mieux retenus que ceux faiblement chargés. La nature de l'ion associé au cation métallique influe également sur le taux de rejection; par exemple, un ion associé à un sulfate SO_4^{2-} sera mieux retenu qu'avec un nitrate NO_3^-.[24]

—les propriétés physiques du sel: l'encombrement stérique est un facteur important dans le passage de type capillaire. A fonction chimique identique, le taux de rejet décroît avec le poids moléculaire.[25] La configuration spatiale joue également un rôle important.[26–30]

Tous ces paramètres physico-chimiques agissent simultanément et sont interdépendants. On pourra agir préférentiellement sur les uns ou les autres par des conditions expérimentales et l'utilisation de solutés appropriés.

Nous nous proposons d'étudier ici l'influence de divers complexants sur le mécanisme de transfert à travers une membrane en fonction de leurs propriétés physico-chimiques (pouvoir donneur ou accepteur de liaisons hydrogène, propriétés hydrophyles ou hydrophobes, affinité pour la membrane, etc.).

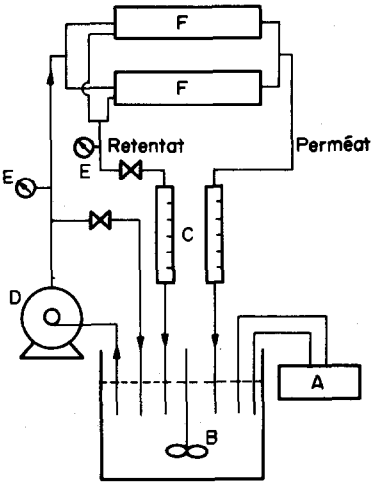


Fig. 1. Schéma du pilote d'osmose inverse: A: régulation IPL de pH; B: agitateur; C: débitmètres; D: pompe; E: manomètres; F: modules de membranes tubulaires.

CONDITIONS EXPERIMENTALES

Cette étude a été effectuée sur une unité comprenant deux modules à membranes de polyamides aromatiques Dupont de Nemours. Le débit peut varier de 200 à 700 l./h; le pH est suivi et régulé par un système IPL Merlin Gerin (Fig. 1).

Les solutions sont préparées avec 50 litres d'eau osmosée. La concentration en cations métalliques est de $10^{-3}M$. Pour les dosages des métaux, nous employons un spectrophotomètre d'adsorption atomique Techtron 100. Les différents complexants ajoutés sont à une concentration constante égale à $10^{-2}M$.

La pression appliquée varie de 9 à 28 bars, la conversion variant de 10 à 90%. L'élévation de température due au passage dans la pompe et au circuit fermé est de quelques degrés. Des essais préliminaires ont montré qu'elle n'avait qu'une influence négligeable sur les performances du système.

RESULTATS EXPERIMENTAUX

Pour chaque essai, nous suivons la concentration en cation métallique dans la solution initiale, le rétentat et le perméat.

Les résultats sont caractérisés par:

—taux de conversion:

$$Y = (Q_p/Q_i) \times 100$$

avec Q_p = débit du perméat,

Q_i = débit initial;

–taux de rejet:

$$R = \left(1 - \frac{C_p}{C_i}\right) \times 100$$

$$= 1 - SP$$

avec C_p = concentration en cation du perméat,

C_i = concentration en cation de la solution initiale.

SP = passage de sel.

Des essais ont été faits avec le cuivre en présence de triéthanolamine. Sur la figure 2, on observe que l'ajout de complexant diminue considérablement le taux de rejet. Le complexant seul traverse également la membrane.

Nous avons effectué des essais analogues avec le cuivre et les complexants suivants: EDTA (Fig. 3); acide citrique (Figs. 4 et 5); acétylacétone (Fig. 6); glycine, acide formique et acétique (Tableau 1).

Dans tous les cas, le passage du cuivre seul est indépendant du pH. Au contraire, la migration du complexe cuivrique est fortement influencée par le pH. Par contre, des essais sur des complexants tels la butylamine, la tétraéthylènepentamine n'ont montré qu'une influence négligeable sur le transfert des ions cuivriques.

Nous avons aussi utilisé d'autres cations métalliques avec les mêmes complexants: les comportements du nickel et de l'argent sont très voisins de celui du cuivre. Par contre, l'étain présente un comportement opposé. En présence d'acétylacétone, son taux de rejet avoisine les 100%.

Nous n'avons observé aucun phénomène de synergisme par l'addition d'un autre cation métallique (Ni, Sn).

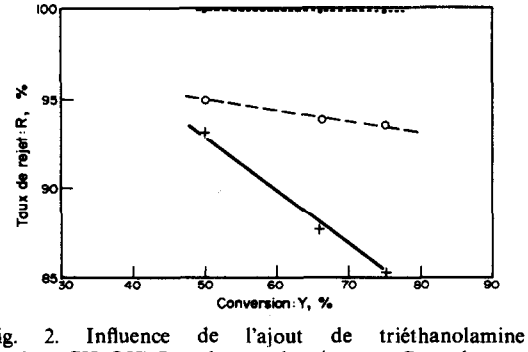


Fig. 2. Influence de l'ajout de triéthanolamine [$N(CH_2\text{-}CH_2OH)_3$] sur le taux de rejet: ....: Cu seul; ---: Triéthanolamine seule; ——: Triéthanolamine + Cuivre.

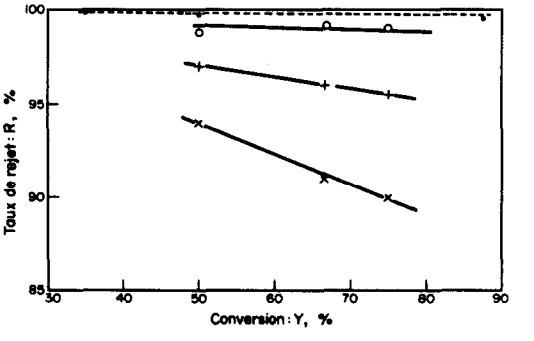


Fig. 3. Influence de l'ajout de l'acide ethylène diamine tetra acétique [$(HOOC\text{-}CH_2)_2N—CH_2CH_2—N(CH_2\text{-}COOH)_2$] sur le taux de rejet, à différents pH; ....: Cu seul; ——: Cu + EDTA; × pH = 2,2; + pH = 4,4; ○ pH = 10,2.

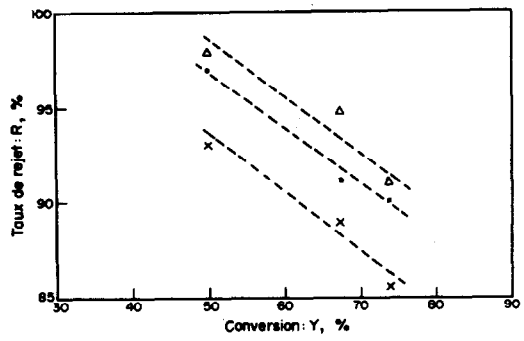


Fig. 4. Variation du taux de rejet de l'acide citrique [$C_3H_4(OH)(COOH)_3 = H_4L$] en fonction de la conversion, pour différents pH: ×: pH = 3; ○: pH = 4,5; Δ: pH = 7.

La détermination des concentrations en sels, dans la solution initiale, le perméat et le rétentat, a permis d'effectuer un bilan matière à chaque essai. On a pu ainsi mettre en évidence une certaine adsorption du cation métallique sur la membrane, au début de chaque essai.

D'autre part, on constate, avec l'ajout de complexant, une augmentation du débit de solvant au travers de la membrane, et ceci d'autant plus que le pH est faible.

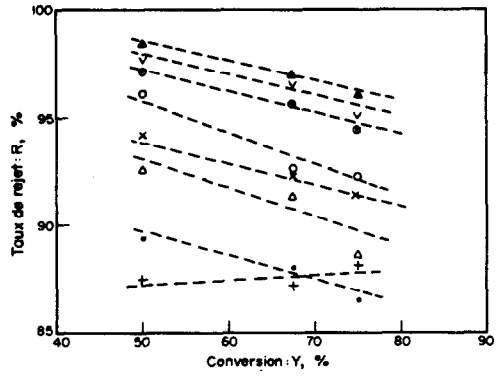


Fig. 5. Variation du taux de rejet du cuivre, en présence d'acide citrique, pour différents pH: Δ: pH = 3; v: pH = 3,2; ⊙: pH = 3,6; ○: pH = 3,8; ×: pH = 4; Δ: pH = 4,5; ·: pH = 5; +: pH = 6,5.

DISCUSSION

Par l'ajout de complexants organiques, on peut agir sur le flux de solvant et/ou sur le flux de sel.

Flux de solvant

En osmose inverse, le flux de solvant traversant une membrane est donné par l'expression:

$$J_1 = \frac{DC}{RT}\frac{V}{\Delta x}(\Delta P - \Delta\pi) = A(\Delta P - \Delta\pi)$$

avec D = coefficient de diffusion du solvant dans la membrane;
C = concentration moyenne du solvant dans la membrane;
V = volume molaire partiel du solvant;
Δx = épaisseur effective de la membrane;
ΔP = différence de pression hydrostatique de part et d'autre de la membrane;
$\Delta\pi$ = différence de pression osmotique de part et d'autre de la membrane;
A = perméabilité de la membrane au solvant.

Tableau 1. Influence de l'ajout de glycine [NH_2—CH_2—COOH], d'acide formique [HCOOH], d'acide acétique [CH_3COOH] sur le rejet du cuivre, à différents pH

Nature du soluté	pH	$Y = 50$	$Y = 66$	$Y = 75$
Cuivre seul	—	99,7–99,5	99,5–99,3	99,2–99
Cuivre + acide formique	3,2	82	73	68
	4,0	70	72	73
	4,3	80	74	72
	5,7	98	90	86
Cuivre + glycine	4,4	81	87	84
	7,6	93	90	88
	8,2	94	91	89
Cuivre + acide acétique	4,3	91	90	89
	5,0	94	92	92
	6,9	99,5	99,5	99

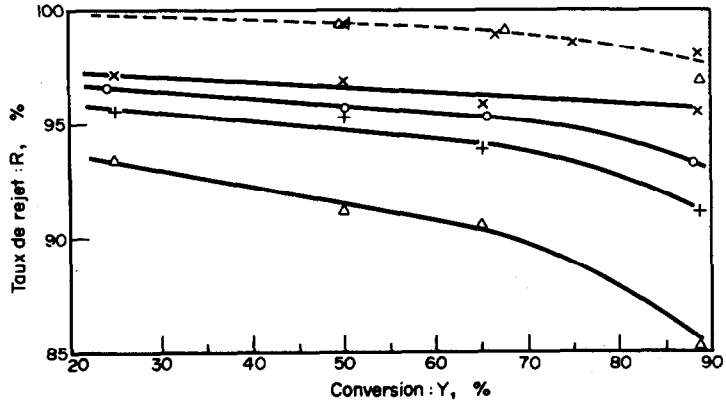


Fig. 6. Influence de l'ajout d'acétylacétone [$CH_3COCH_2COCH_3 = HL$] sur le taux de rejet, à différents pH: ....: Cu seul; ——: Cu + acétylacétone; Δ: pH = 3; +: pH = 5; ·: pH = 6,4; ×: pH = 7.

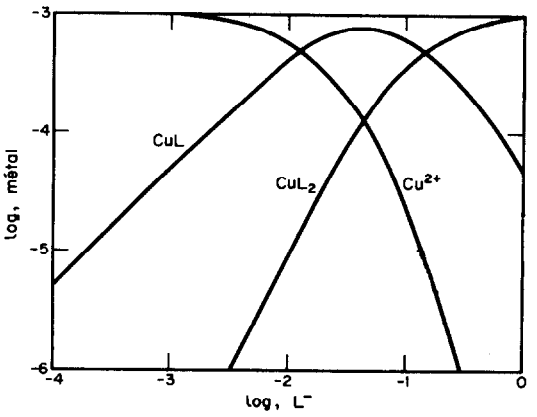


Fig. 7. Diagramme de répartition des complexes cuivre–acétylacétone en fonction du log (acétylacétone total), à pH = 7, à force ionique variable.

L'ajout du complexant entraîne généralement une augmentation du flux d'eau, à pression et conversion données; l'addition d'un solvant soluble à la fois dans l'eau et dans la membrane augmente la solubilité de l'eau dans la membrane (C dans la formule précédente). La membrane se comportant comme un solvant non aqueux, ceci s'accorde bien avec ce que l'on observe en général dans ces milieux.

Flux de sel

Le flux de sel traversant la membrane est donné par l'expression:

$$J_s = \frac{D_s K}{\Delta x} \Delta C = B.\Delta C$$

avec D_s = coefficient de diffusion du soluté dans la membrane;
K = coefficient de partage (ou de distribution) du soluté entre la membrane et la solution;
Δx = épaisseur effective de la membrane;
ΔC = différence de concentration de part et d'autre de la membrane;
B = perméabilité du sel.

Par l'ajout de complexants organiques, on peut modifier le coefficient de partage K.

Influence des liaisons hydrogènes entre membrane et produit diffusant

Le transfert à travers la membrane est lié au coefficient de partage du produit diffusant, donc à sa solubilité dans celle-ci. Cette solubilité est très fortement dépendante de la possibilité de former des liaisons hydrogènes entre membrane et produit diffusant.[13–15]

La membrane que nous avons utilisée est en polyamides aromatiques dont le pouvoir accepteur de liaisons hydrogènes est marqué. De ce fait, les produits fortement donneurs de liaisons hydrogènes (acides carboxyliques, alcools, etc.) migrent beaucoup mieux que ceux avant un pouvoir accepteur (amines).

Tableau 2. Répartition des complexes cuivre–EDTA en fonction du pH, à la concentration d'EDTA de $10^{-2}M$

pH	Cu^{2+}	$CuYH^-$	CuY^{2-}
2,25	4.10^{-8}	$8{,}5.10^{-4}$	$1{,}5.10^{-4}$
4,45	$1{,}5.10^{-9}$	3.10^{-5}	10^{-3}
10,20	—	—	10^{-3}

Tableau 3. Répartition des complexes cuivre–acide citrique en fonction du pH, à la concentration d'acide citrique de $10^{-2}M$

pH	pK'	Cu^{2+}	$CuHL^-$
3	3,1	$1{,}3.10^{-4}$	$8{,}7.10^{-4}$
3,6	2,5	$3{,}8.10^{-4}$	$6{,}2.10^{-4}$
5	1,1	$9{,}4.10^{-4}$	$5{,}7.10^{-5}$
5,7	−0,4	10^{-3}	$1{,}9.10^{-6}$

Certains complexants ont leur passage facilité par leur caractère à la fois donneur et accepteur de liaisons hydrogènes.[3] On peut penser que leur solubilité dans la membrane est augmentée par des associations en chaines.

Influence de la nature des complexes métalliques

En ce qui concerne le transfert des complexes métalliques, il est important de connaître leur nature et leur stochiométrie. Pour cela, nous avons tracé les diagrammes de répartition des complexes, pour un métal, en fonction de la concentration en ligand[32,33] (Fig. 7).

Pour les complexes avec l'EDTA et l'acide citrique, par exemple, les répartitions des complexes aux pH utilisés sont regroupées dans les tableaux 2 et 3.

On remarque ainsi (Figs. 3 et 5) que le maximum de transfert correspond à un maximum de concentration des complexes protonés ($CuYH^-$ et Cu Cit H). Ici encore, le pouvoir donneur de liaisons hydrogènes du complexe formé est un facteur prépondérant pour faciliter le transfert; ce sont en effet les

Tableau 4. Répartition des complexes cuivre–acétylacétone en fonction du pH, à la concentration d'acétylacétone de $10^{-2}M$

pH	Cu^{2+}	CuL	CuL_2
3	5.10^{-4}	5.10^{-4}	10^{-5}
5	$3{,}9.10^{-6}$	$2{,}5.10^{-4}$	$7{,}4.10^{-4}$
6,4	5.10^{-9}	10^{-5}	10^{-3}
7	10^{-9}	$2{,}5.10^{-8}$	10^{-3}

Tableau 5. Répartition des complexes cuivre–acide acétique en fonction du pH, à la concentration d'acide acétique de $10^{-2}M$

pH	Cu^{2+}	CuL	CuL_2	CuL_3^-	CuL_4^{2-}
4,3	$9{,}7.10^{-4}$	$2{,}6.10^{-5}$	$3{,}3.10^{-7}$	$2{,}1.10^{-9}$	5.10^{-12}
5	$9{,}2.10^{-4}$	$7{,}7.10^{-5}$	$2{,}5.10^{-6}$	$3{,}1.10^{-8}$	$2{,}4.10^{-10}$
7	9.10^{-4}	9.10^{-5}	$3{,}8.10^{-6}$	7.10^{-8}	8.10^{-10}

Tableau 6. Répartition des complexes cuivre–acide formique en fonction du pH, à la concentration d'acide formique de $10^{-2}M$

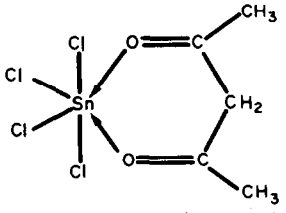
pH	Cu^{2+}	$CuHCO_2$
3,2	$1,4.10^{-5}$	$8,5.10^{-4}$
4,0	$3,6.10^{-4}$	$6,4.10^{-4}$
4,3	$2,2.10^{-4}$	$7,8.10^{-4}$

complexes protonés qui ont le passage le plus important.

Les répartitions des complexes pour l'acétylacétone, l'acide acétique et l'acide formique sont regroupées dans les tableaux 4–6.

Pour ces complexants, on observe un maximum de transfert correspondant à un domaine où le cuivre n'est pas ou peu complexé. On peut penser que dans la membrane les cations métalliques sont fortement solvatés par le ligand LH, ce qui favorise leur solubilité dans la membrane, donc leur transfert. Le caractère donneur de liaisons hydrogènes est donc ici un facteur prépondérant par rapport aux facteurs ioniques et stériques.[22]

Pour le cas particulier de l'étain, en présence d'acétylacétone, la structure particulière du complexe formé[34] explique son comportement opposé.



En effet, la forme cétone du complexant que l'on observe ici est accepteuse de liaisons hydrogènes et ne favorise pas le transfert; par contre, l'accroissement du volume du soluté par formation de complexe diminue la vitesse de diffusion et le transfert de l'étain est alors plus faible quand il est complexé par l'acétylacétone.

Mécanisme de transfert des complexes

Pour interpréter les mécanismes de transfert globaux, la perméabilité partielle B des différentes espèces a été calculée. Soit la relation:

$$J_s = B(C_i - C_p)$$

avec J_s = flux de sel par unité de surface de membrane;
B = perméabilité du sel;
C_i = concentration dans la solution initiale;
C_p = concentration dans le perméat.

Tableau 7. Valeurs des perméabilités partielles des différents complexes de l'EDTA, pour différentes conversions

Y,%	Cu^{2+}	$CuYH^-$	CuY^{2-}
50	$0,2.10^{-4}$	41.10^{-4}	25.10^{-4}
66	$0,3.10^{-4}$	65.10^{-4}	24.10^{-4}
73	$0,4.10^{-4}$	68.10^{-4}	25.10^{-4}

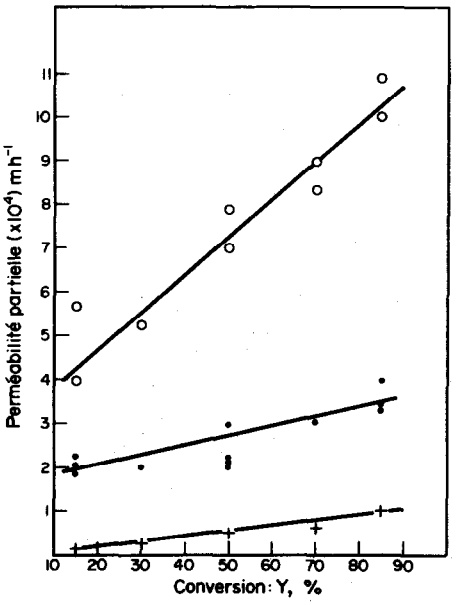


Fig. 8. Variation des perméabilités partielles en fonction de la conversion—cas de l'acétylacétone. +: perméabilité partielle du cuivre seul; ·: perméabilité B_2 de l'espèce CuL_2; O: perméabilité B_1 de l'espèce (Cu^{2+}, CuL).

$$J_s = C_p.J_1$$

avec Q_1 = Debit de perméat.

On obtient ainsi:

$$B = J_1.Y.SP/R$$

avec SP = passage de sel.

Nous avons essayé d'atteindre les valeurs des perméabilités partielles de chaque espèce en posant la relation suivante:

$$(Cu)t.B = B_0(Cu^{2+}) + B_1(CuL) + B_2(CuL_2) + \ldots + B_n(CuL_n)$$

Les valeurs des perméabilités partielles pour les complexes cuivre–EDTA sont condensées dans le tableau 7. On remarque qu'en présence de complexant, elles sont 100 à 200 fois supérieures à celles trouvées pour le cuivre seul.

Tableau 8. Variation des perméabilités partielles en fonction de la pression, pour trois conversions de deux espèces: CuL_2 et (CuL–Cu^{2+})

Conversion:	Perméabilité partielle, 10^4 m/h 13%		50%		83%	
Espèce \ Pression, *bars*:	16	28	16	28	19	28
	1,2	2,0	2,0	2,2	3,4	3,4
CuL_2	1,4	1,8	1,9	3,0	3,2	3,7
		1,9		2,9	2,9	
	2,1	4,0	3,6	7,0	6,2	13,2
Cu^{2+}–CuL	2,2	3,9	3,5	6,8	6,1	10,6
	2,1		3,2		6,0	10,2
			3,0			

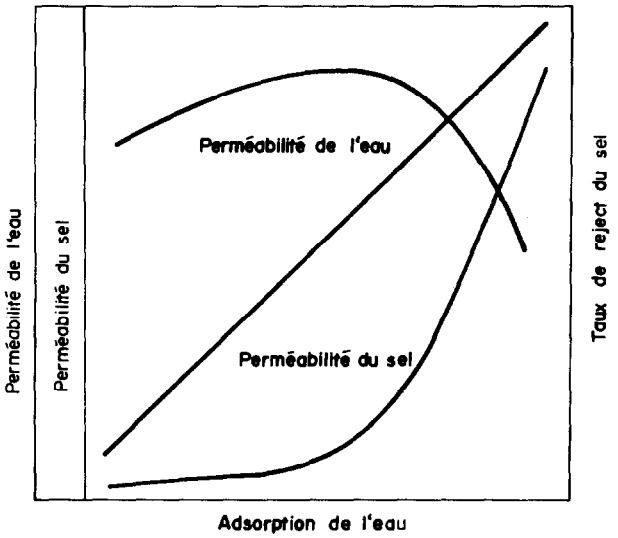


Fig. 9. Variation de la perméabilité du sel et de l'eau, et du taux de rejet du sel, en fonction de l'adsorption d'eau sur la membrane.

L'importance de la configuration stérique et de l'encombrement du sel sur les performances sont connues:[26–29] la grande taille du complexant n'est pas ici le facteur limitant. L'action du ligand influence essentiellement la valeur du coefficient de partage K. L'augmentation de la taille du sel diminue la constante de diffusion, mais augmente surtout la solubilité dans la membrane, phénomène que l'on observe egalement en extraction liquide–liquide, et c'est ce facteur que est prépondérant.

En calculant les perméabilités partielles, pour l'acétylacétone, dans l'hypothèse des trois espèces Cu^{2+}, CuL^{+} et CuL_2, nous obtenons des systèmes de 3 équations à 3 inconnues. Le calcul des perméabilités partielles, à une conversion et une pression données, conduit, dans cette hypothèse, à des résultats aberrants.

Si l'on considère maintenant l'existence de deux seules espèces en solution, on a la relation:

$$B = B_1(Cu^{2+}, CuL) + B_2(CuL_2).$$

Les différents systèmes à deux inconnues conduisent à des valeurs de perméabilité partielles dont la variation en fonction de la conversion est portée sur la figure 8.

Cette équation semble être une bonne interprétation des phénomènes. La première espèce ne serait pas un complexe simple, mais une solvatation préférentielle du cuivre par l'acétylacétone dans la membrane.

Par ailleurs, on peut remarquer que les courbes représentatives de la perméabilité des espèces Cu^{2+} et CuL_2 sont parallèles, alors que celle de l'espèce solvatée présente une pente beaucoup plus forte. Ceci semble montrer que Cu^{2+} et CuL_2 répondent au même mécanisme. Dans l'autre cas, un mécanisme différent vient s'ajouter.

Par ailleurs, on peut remarquer (Tableau 8) que le premier mécanisme est pratiquement indépendant de la pression, ce qui permet de penser qu'il s'agit d'un mécanisme essentiellement de type diffusionnel, alors que dans le second cas la forte influence de la pression laisse penser à la collaboration d'un autre type de mécanisme pouvant être dû à une modification physico-chimique du solvant membranaire.

Influence de la solvatation de la membrane

L'influence de la plus ou moins forte hydratation de la membrane a été décrite par de nombreux auteurs.[16–20]

La variation de la perméabilité des solutés en fonction de l'adsorption d'eau sur une membrane est représentée sur la figure 9. Pour les faibles hydratations, l'adsorption des solutés en membrane est assez faible et pratiquement indépendante de l'adsorption de l'eau; puis, à partir d'un certain point, on observe une augmentation rapide du transfert. Dans cette deuxième partie, l'influence de la pression sur le transfert devient très importante. Dans notre cas, le ligand ajouté solvate la membrane beaucoup mieux que l'eau, ce qui permet de le situer dans la deuxième partie de la courbe.

Le passage du cuivre en présence d'acétylacétone en milieu acide à des pH où il n'est pas complexé peut donc s'interprèter par une très forte solvatation de la membrane, en même temps que des ions cuivriques. De même, l'influence de la pression sur ce passage est dûe à une forte solvatation qui donne un mécanisme de transfert correspondant à la deuxième partie de la courbe d'hydratation (figure 9).

En ce qui concerne l'acide formique et l'acide acétique, le mécanisme de transfert est du même type. On peut, par ailleurs, remarquer que cette forte solvatation de la membrane se produit avec des complex-

ants fortement donneurs de liaisons hydrogènes. Il ne s'agit plus de véritables phénomènes de complexation, mais d'un effet de solvant.

CONCLUSION

De tous les facteurs pouvant influencer le transfert des cations métalliques à travers une membrane d'osmose inverse (effet stérique, vitesse de diffusion, etc.) c'est la solubilité dans la membrane et la forte solvatation de celle-ci qui sont les facteurs prépondérants. L'addition de complexant ou de solvant ayant une grande affinité pour la membrane peut ainsi augmenter d'une façon notable le transfert des cations métalliques.

La complexation sélective ou la différence de structure des complexes formés des divers cations métalliques d'un mélange peut ainsi permettre d'espérer la séparation de ces cations.

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Summary—The influence of complexation by different ligands on the transfer of metallic cations in reverse osmosis has been studied by using membranes composed of aromatic polyamides. In spite of the large volume increase of the diffusing solute, the addition of a complexant can significantly improve the transfer of metallic cations through a reverse osmosis membrane. The most important factor in the improvement of the transfer is the solubility in the membrane of the complexes created. This solubility is linked to the possibility of creating hydrogen bonds between the membrane and the complex. Moreover, the addition of substances which strongly solvate both the membrane and the solute leads to an improvement of transfer which increases considerably with the increasing pressure. These results suggest the possibility of separating metal cations by specific complexation.

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A REVISED METHOD, AND ERRORS IN THE DETERMINATION OF THIOSULPHATE BY THE WOLLAK METHOD

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Summary—The Wollak method for the determination of thiosulfate has been investigated. The experimental procedure has been revised in order to eliminate several problems associated with the method.

In a recent paper,[1] it was demonstrated that the first titration in the Wollak procedure (which determines the sum of dithionite and thiosulphate in a mixture of oxy-sulphur compounds) was susceptible to error if a sample containing dithionite, thiosulphate and bisulphite produces a solution with pH <7 when added to an aqueous formaldehyde solution neutralized to Methyl Orange as originally suggested by Wollak.[2] Under acidic conditions, thiosulphate reacts with formaldehyde. The rate of reaction is dependent on the pH, the formaldehyde concentration and the thiosulphate concentration. This problem can be eliminated by the addition of enough sodium hydroxide or carbonate to the aqueous formaldehyde to maintain the pH of the sample–formaldehyde solution above 7.

The subject of this report is the determination of thiosulphate by the second titration in the Wollak procedure. Zocher and Saechtling[3] concluded that this method was unsatisfactory, whereas Murooka[4] found the approach satisfactory. This titration was also studied by Latimer,[5] who reported difficulty in detection of a suitable end-point in the iodine titration and found that the thiosulphate determination could produce high results. This can occur when the initial oxidation takes place in a solution that is too acidic ($>1M$ H^+), a situation that can develop if the thiosulphate content of a mixture is less than 10%. On the other hand, Danehy and Zubritsky[6] have recently reported analyses of mixtures of oxy-sulphur compounds by the Wollak method and have found the procedure "unexceptionable".

Owing to the diversity of reports concerning the determination of thiosulphate, the Wollak procedure has now been reinvestigated. The experimental procedure has been found to be totally unacceptable.

The purpose of this report is to illustrate the nature of the problem encountered and to develop an experimental procedure by which an accurate determination of thiosulphate can be obtained in the presence of dithionite and bisulphite.

THEORY

Thiosulphate is determined in the presence of dithionite and bisulphite by adding the mixture to an acidified excess of iodine solution. The following reactions occur.

$$S_2O_4^{2-} + 3I_2 + 4H_2O \rightarrow 2HSO_4^- + 6HI \quad (1)$$

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \quad (2)$$

$$HSO_3^- + I_2 + H_2O \rightarrow HSO_4^- + 2HI \quad (3)$$

Excess of sulphite solution is then added to remove any unreacted iodine in accordance with equation (3) and (after the pH has been adjusted to between 8 and 10) to convert the tetrathionate, $S_4O_6^{2-}$, quantitatively into half the original amount of thiosulphate according to the reaction

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S_3O_6^{2-} \quad (4)$$

The unreacted sulphite is complexed by the addition of formaldehyde and acetic acid.

$$SO_3^{2-} + CH_2O \xrightarrow{H+} CH_2OHSO_3^- \quad (5)$$

The thiosulphate produced by the reaction (4) is then titrated with standard iodine solution.

EXPERIMENTAL

Reagents

Reagent-grade chemicals and distilled water were used throughout. Thiosulphate solutions were standardized with standard potassium iodate solution and used in turn to standardize the iodine solutions. The sulphite solution was prepared from the anhydrous salt without deaeration and was approximately 10% w/v (0.8M). Sodium acetate trihydrate and purified dithionite (J. T. Baker Co.) were used throughout the work. The sodium dithionite contained 2.53% thiosulphate (determined as explained above).

Procedure

In theory, the Wollak method for the analysis of thiosulphate is acceptable, but the experimental procedure has been found to be totally unacceptable for reasons which

will be enumerated in the discussion. A revised experimental procedure is now described.

Add 0.4 g of a thiosulphate-containing dithionite sample through a dry long-stemmed funnel to about 73 ml of iodine solution (made by mixing 15 ml of 0.5*M* iodine with 60 ml of water and dissolving at least 3 g, preferably 4, of sodium acetate in it) in a 100-ml standard flask, adding the sample slowly with constant swirling of the solution, during 30–60 sec (this should give a slight excess of iodine, 70 ml being enough for 0.4 g of dithionite). Rinse in any residue from the funnel with the rest of the iodine/acetate solution. Remove the unreacted iodine by addition of 0.8*M* sodium sulphite solution and add 8–10 ml more sulphite solution immediately and rapidly. Neutralize the solution to phenolphthalein (pH 8–10) by dropwise addition of 10*M* sodium hydroxide, let stand for 5 min, then add 4 ml of 37% formaldehyde and about 5 ml of 20% acetic acid. Dilute to the mark with water. Remove a 25- or 50-ml aliquot, adjust the pH to 4 with 20% acetic acid, and titrate with 0.005*M* iodine from a microburette, to a sharp end-point with starch. The end-point colour will be violet owing to the presence of formaldehyde.

DISCUSSION

Sodium acetate was originally added to the iodine solutions to control the pH and prevent the decomposition of dithionite by the hydriodic acid produced. The relationship between the sodium acetate concentration, pH and recovery of thiosulphate was studied by means of the following experiments.

Mixtures of various oxy-sulphur compounds were prepared by adding known amounts of anhydrous sodium bisulphite and anhydrous sodium thiosulphate to a previously analysed sample of sodium dithionite. The preweighed mixtures were added to excess of standard iodine solution containing various amounts of sodium acetate and the pH was recorded.

The effect of pH on the initial iodine oxidation of thiosulphate was determined by adding 0.1–0.3 g of anhydrous thiosulphate to buffered iodine solutions (iodine in excess) containing appropriate amounts of hydrochloric acid, acetic acid–acetate buffer or sodium acetate to give a total volume of 50 ml of 0.05 or 0.1*M* iodine. The effects of pH on the recovery of thiosulphate in mixtures of oxy-sulphur compounds were determined by adding known amounts of analysed sodium dithionite and sodium dithionite–thiosulphate mixtures to excess of iodine in solutions containing various amounts of sodium acetate. In both studies, the thiosulphate was then determined by the revised method.

The decomposition of dithionite appears to produce sulphide,[2,7] and since formation of sulphur also occurs at low pH, it was decided that several sulphide reactions should be investigated as a possible explanation for the formation of sulphur and the positive errors found for thiosulphate at low pH. Since the reaction of sulphide with various constituents might be competitive with the oxidation of sulphide by iodine, the study was made under the most favourable conditions, *i.e.*, with excess of sulphide and in the absence of iodine. Excess of ultrapure sodium sulphide from an unopened bottle was added to a known amount of sodium tetrathionate (99% pure) dissolved in various acid solutions of differing pH. The reaction was allowed to proceed for 5 min and excess of cadmium chloride was then added. The cadmium sulphide was filtered off and washed and the filtrate titrated with 0.05*M* iodine. A correction was applied for the oxidizable impurity in the tetrathionate. The experiment was repeated with sodium sulphite in place of the tetrathionate. In this case, formaldehyde was added before titrating with iodine.

A pH-dependent reaction of formaldehyde bisulphite with iodine was investigated as a possible cause of the fading end-point previously reported by Latimer.[5] Known amounts of anhydrous sodium bisulphite were added to aqueous solutions containing 4 ml of 37% formaldehyde solution in 100-ml volumetric flasks. The solutions were diluted to the mark, 25-ml aliquots were withdrawn, starch indicator was added and the aliquots were buffered at various pH values between 4 and 7, then titrated with 0.005*M* iodine. Acidified formaldehyde was also titrated to obtain a blank.

The Wollak method

The determination of thiosulphate by the Wollak method has been found to be unacceptable for the following reasons. The major problem arises in titration of the final solution. When a 0.2-g sample of sodium dithionite was analysed for thiosulphate by the method suggested by Wollak[2] and recently by Danehy and Zubritsky,[6] the end-point was found to occur on the addition of a few drops of 0.05*M* iodine. If 0.005*M* iodine was used, then the end-point was not detectable because of dilution of the iodine in the large volume of solution,[8] combined with the presence of formaldehyde which hinders the detection of the starch–iodine end-point. In addition, the 1 g of sodium acetate originally added to prevent the acid decomposition of dithionite is insufficient in samples containing relatively large amounts of dithionite. The revised experimental procedure eliminates these problems, including the fading end-point previously reported.[5]

Table 1 shows the pH to be expected when mixtures of oxidizable sulphur compounds are added to various iodine–sodium acetate solutions. The hydrogen ion is generated in the iodine oxidation of bisulphite and dithionite.

The initial step of the Wollak titration (either the original or the revised method), is equivalent to a titration of the thiosulphate with iodine under conditions of acidity determined by the composition of both the sample and the oxidizing solution. The effect of pH on the recovery of thiosulphate is illustrated in Fig. 1 and tabulated in Table 2. The low recovery at higher pH is attributable to the partial oxidation of thiosulphate to sulphate.[8] Although the literature indicates quantitative recovery of thiosulphate by use of excess of iodine (concentration not reported) with

Table 1. pH of various mixtures* of sulphur oxy-anions after oxidation in sodium acetate/iodine solutions

$Na_2S_2O_4$, %	$Na_2S_2O_3$, %	$NaHSO_3$, %	pH A	pH B	pH C
89.9	2.5	6.9	1.97	1.02	3.92
85.1	7.6	6.5	—	1.10	3.99
68.6	24.9	6.0	3.54	1.21	4.29
68.6	6.0	24.9	2.30	1.11	4.08
49.8	44.8	5.0	4.23	1.54	4.62
49.8	5.0	44.8	2.87	1.13	4.19
10.0	79.7	10.0	5.12	4.62	5.36
10.0	10.0	79.9	3.93	1.39	4.43
—	50.0	50.0	4.68	3.65	4.93
—	100.0	—	6.99	7.06	7.26
—	—	100.0	3.83	1.32	4.40

* The mixtures were prepared by adding known amounts of anhydrous $Na_2S_2O_3$ and $NaHSO_3$ to an analysed sample of sodium dithionite containing 89.9% $Na_2S_2O_4$. 2.53% $Na_2S_2O_3$, 6.88% $NaHSO_3$, and calculating the final composition. The remainder consists of a small amount of formate and chloride impurity.

A—0.2 g of sample in 75 ml of 0.05*M* I_2 containing 1.0 g of sodium acetate.

B—0.4 g of sample in 75 ml of 0.1*M* I_2 containing 1.0 g of sodium acetate.

C—0.4 g of sample in 75 ml of 0.1*M* I_2 containing 3.0 g of sodium acetate.

pH as low as −0.5,[9] Fig. 1 shows that high thiosulphate recovery can occur at pH ~1. This may be the result of using different iodine concentrations.

Analysis of a sample of sodium dithionite gave the same behaviour as when thiosulphate was oxidized by acidic iodine, *i.e.*, high thiosulphate recovery from solutions of low pH. The results are tabulated in Table 3. The high standard deviation at low pH is indicative of the unreliability of the analysis when insufficient sodium acetate is present. Positive errors for thiosulphate are invariably accompanied by the formation of sulphur during the initial oxidation. The

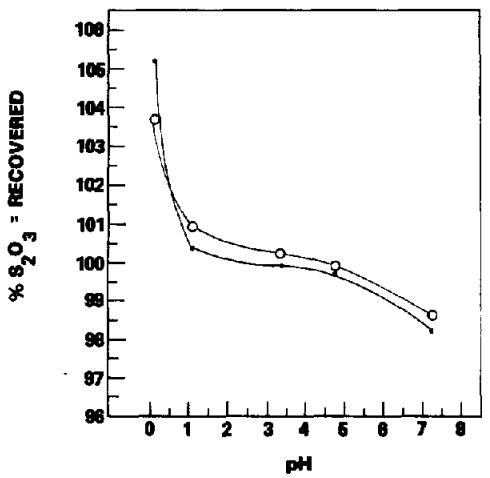

Fig. 1. The effect of pH on the recovery of thiosulphate (%) in buffered solutions containing (*a*) ○ 0.05*M* I_2, (*b*) ● 0.1*M* I_2.

Table 2. The effect of pH on the recovery (%) of thiosulphate in the Wollak procedure

pH	0.05*M* I_2	0.1*M* I_2
0.5	103.7 (n = 2, S = 0.3)*	105.2 (n = 4, S = 1.0)
1.10	100.9 (n = 2, S = 0.3)	100.4 (n = 2, S = 0.3)
3.35	100.2 (n = 2, S = 0.6)	99.9 (n = 2, S = 0.6)
4.76	99.8 (n = 3, S = 0.4)	99.7 (n = 3, S = 0.4)
7.26	98.6 (n = 5, S = 1.0)	98.2. (n = 3, S = 0.4)

* n = number of 0.1-g samples (3 titrations per sample); S = standard deviation.

amount of sulphur appears to be proportional to the excess of thiosulphate found, though this has not been confirmed.

Some of the potential causes of the high thiosulphate results and sulphur formation were briefly examined.

(*i*) The intensity of the yellow colour that appears on addition of excess of sulphite during the removal of the excess of iodine was found to be pH-dependent, being most intense at low pH (0–2) and increasing with iodine and/or bisulphite concentration. However, the addition of sulphite to dithionite samples did not affect the recovery of thiosulphate. Also, sulphite added to excess of sulphide in iodine medium at pH 0.8 did not produce any thiosulphate. Neither the yellow complex nor sulphite under acidic conditions appears to be a direct factor. Latimer has shown that a sulphur–sulphite reaction cannot account quantitatively for increases in the amount of thiosulphate found.

(*ii*) Tetrathionate, the only reactive oxidant that is formed by oxidation with iodine, was investigated. The reaction between excess of sulphide and tetrathionate

$$S^{2-} + S_4O_6^{2-} \rightarrow S + 2S_2O_3^{2-} \qquad (6)$$

was studied in the absence of iodine and found to result in 1.3, 6.4 and 93% conversion into thiosulphate at pH values of 0.8, 1.0, 4.8 respectively. Although increasing pH favours the reaction of tetrathionate

Table 3. The effect of pH of the initial iodine oxidation in the Wollak procedure on the recovery (%) of thiosulphate in sodium dithionite

CH_3COONa, *g*	pH*	$Na_2S_2O_3$, %	S†, %	n§
0	0.80	4.35	0.37	6
1.0	1.01	3.20	0.40	17
1.5	1.27	2.74	0.16	5
2.0	1.69	2.67	0.19	8
3.0	4.00	2.53	0.11	6
4.0	4.36	2.52	0.054	5

* Average pH recorded after the oxidation of a known mass (0.4 g) of sodium dithionite in 75 ml of 0.1*M* I_2 containing the amount of sodium acetate shown.

† S = standard deviation.

§ n = number of samples analysed (revised Wollak method), two titrations per sample.

Table 4. The effect of pH and a standard addition of thiosulphate on the determination of thiosulphate in sodium dithionite

CH_3COONa, g	$S_2O_4^{2-}$*, g	$S_2O_3^{2-}$*, g	pH†	$S_2O_3^{2-}$, %	$S_2O_3^{2-}$ in $S_2O_4^{2-}$, %	S§, %
0	0.4029	0.02244	0.82	9.44	4.40	1.03
1	0.3998	0.02254	1.04	8.56	3.40	0.65
2	0.4025	0.02306	1.68	7.84	2.56	0.12
3	0.4030	0.02264	3.96	7.62	2.43	0.051
4	0.4021	0.02242	4.39	7.54	2.40	0.029

* Average masses of anhydrous sodium thiosulphate and sodium dithionite (4 samples).

† pH of approximately 75 ml of 0.1*M* I_2 containing the stated amount of sodium acetate after both the $S_2O_4^{2-}$ and $S_2O_3^{2-}$ had been added.

§ S = standard deviation for analysis of four samples, two titrations per sample.

and formation of sulphur, the high thiosulphate results that occur at low pH cannot be explained by this reaction.

Acid decomposition of tetrathionate in excess of iodine was examined. After oxidation of a 0.4-g sample of sodium dithionite in excess of 0.1*M* iodine (pH ~4), concentrated hydrochloric acid was added until the pH was 0.8. No sulphur formed and the amount of thiosulphate found (2.48%) was similar to that found by oxidation at pH ~4.

Although high thiosulphate results correlate with oxidation at low pH, hydrolysis of tetrathionate at high pH

$$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \quad (7)$$

and hydrolysis of trithionate produced upon addition of excess of sulphite (reaction 5) have been reported as possible sources of thiosulphate. However, the analytical procedure was found to tolerate large variations in both time of standing and the pH of the sulphite solutions. Tetrathionate was judged not to be a cause of the high thiosulphate results.

(*iii*) The acid decomposition of thiosulphate, which occurs competitively with oxidation, has been proposed as an explanation of the high thiosulphate results at low pH.[9]

In order to examine this possibility, a sample of dithionite, containing approximately 2.5% thiosulphate, was analysed in the presence of an additional 5% of thiosulphate. The results are shown in Table 4. If acid decomposition is the explanation for increased thiosulphate recovery, then it might be expected that still more thiosulphate would be found by the reaction at low pH when more thiosulphate is present. Comparison of the recovery of dithionite (Table 3) and dithionite with additional thiosulphate present (Table 4) is illustrated in Fig. 2. No significant difference is observed. The thiosulphate concentration in itself does not appear to be the major contributing factor. In addition, when the amount of thiosulphate was increased threefold from that reported in Table 2, no significant variation in the recovery of thiosulphate was detected.

Thiosulphate recovery increases with decreasing pH whereas sulphite oxidation with iodine was found

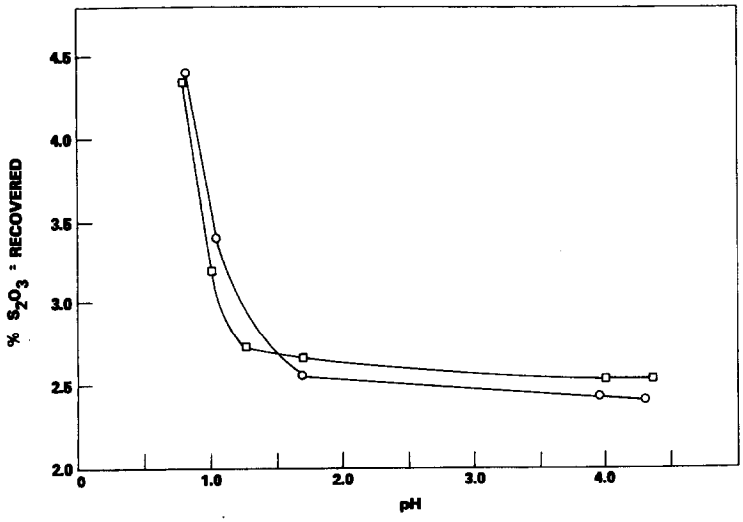

Fig. 2. The recovery of thiosulphate (%) in (*a*) □ a sample of sodium dithionite; (*b*) ○ a sample of sodium dithionite containing an additional twofold amount of thiosulphate.

Table 5. The effect of pH on the total iodine consumed by a sample (0.4 g) of dithionite*

CH_3COONa, *g*	pH	I_2, *mmole*
0	0.92	6.38
1	1.15	6.41
2	1.80	6.43
3	3.94	6.44
4	4.38	6.45

* Three samples of 0.4000 g of sodium dithionite were oxidized with 75 ml of 0.1*M* I_2 at each pH and the average iodine consumed was determined by titrating the unreacted iodine with standard thiosulphate.

to be independent of pH, giving the same recovery at pH 0.25 as at pH 5.15. Consequently, the results of Table 5 show that increasing acidity allows some acid decomposition of dithionite to occur competitively with iodine oxidation. Stoichiometrically, the acid decomposition products of dithionite require less iodine at low pH.

The fading end-point previously reported is the result of a pH-dependent reaction between iodine and formaldehyde bisulphite. The rate of end-point fading in titration of a bisulphite ($\sim 10^{-3}M$) solution containing excess of formaldehyde (4 ml of 37% HCHO in 100 ml) with 0.005*M* iodine increases with increasing pH. The end-point fades rapidly at pH >6 and the precision of analyses is poor if the pH approaches this value. Good reproducible analyses can be performed if the pH is adjusted to 4.0 before the titration.

Conclusion

The Wollak titration of thiosulphate has been modified. The new experimental procedure eliminates the numerous problems cited and allows correct analysis for thiosulphate in the presence of large amounts of other sulphur compounds that can be oxidized with iodine. Several reactions have been examined in order to explain the high thiosulphate results that occur when the pH of the iodine solution is too low, but it is difficult to decide which, if any, is the main cause of the error, though some can be ruled out.

The third titration in the Wollak procedure has also been investigated. When thiosulphate, bisulphite and dithionite are simultaneously oxidized by iodine, sufficient sodium acetate must be added (minimum pH ~4) in order to minimize acidic decomposition of dithionite, which would compete with the iodine oxidation and cause error to arise.

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ANALYTICAL ASPECTS OF ABSORPTION SPECTROELECTROCHEMISTRY AT A PLATINUM ELECTRODE—I
STUDY OF METAL IONS

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Summary—An apparatus has been built with which the intensity of a light-beam passing at grazing incidence over a platinum electrode can be monitored. The absorption of light which occurs during the electrolysis of dilute aqueous metal ion solutions has been studied as a function of a number of parameters including wavelength, potential difference and concentration. The theories of metal deposition and processes occurring at the electrode surface and in the diffusion layer have been examined and a mechanism for the production of the absorbing species in terms of increase in pH of the catholyte is proposed. The analytical potential of the technique is discussed.

The combination of optical techniques such as internal reflection spectroscopy, ellipsometry, transmission spectroscopy, specular reflection spectroscopy, with electrochemical methods such as chronoamperometry, chronopotentiometry and linear sweep voltammetry provides powerful methods for the elucidation of the mechanism of electrode reactions, identification of intermediates, and nature of adsorbed species and the determination of diffusion coefficients and rate constants.[1–3]

From the analytical point of view, those methods in which the concentration of an electroactive species rather than the nature of the electrode surface is monitored during electrolysis, are of interest. These spectroelectrochemical methods are based on the use of an optically transparent electrode (OTE). Two types of electrodes are in common use, namely, (1) thin-film electrodes made by coating a transparent substrate with metals (platinum, gold, silver, mercury)[4–6] or doped oxides (tin oxide or indium oxide)[7–9] and (2) minigrid electrodes usually made by etching rectangular holes in fine metal foils (usually gold).[10] The methods of monitoring the electroactive species at these electrodes are (1) normal transmission spectroscopy (NTS), where the absorbance of a light-beam passing at right angles through the electrode surface is monitored and (2) internal reflection spectroscopy (IRS). The basis of IRS is the fact that when a light-beam undergoes total internal reflection at a phase boundary, the light-beam actually penetrates the rarer medium.[11] Thus, when a beam of light traverses a thin-layer OTE, every time an internal reflection occurs at the film–solution interface, the light-beam passes into the solution for a few nm, where it may be absorbed by species close to the electrode surface. The complete (though somewhat complex) theory for the three-phase case (*i.e.*, glass, film, solution) has been given by Hansen.[1,12]

Normal transmission spectroscopy at thin-film OTEs was first described by Kuwana *et al.*[13,14] The scope of the method is shown in two recent reviews.[2,15] NTS at minigrid OTEs is described by Murray *et al.*[10] These spectroelectrochemical methods have also been used in conjunction with thin-layer cells. These are narrow cells (typically 10^{-2} mm) with a small electrolyte volume (a few μl) so electrolysis becomes exhaustive after a few hundred msec. The theory and applications of these types of cells have been reviewed.[16,17] The use of this type of cell with gold minigrid electrodes is described by Murray[18] and with platinum film electrodes by Reilley.[4]

The combination of IRS and thin film OTEs was first reported by Kuwana *et al.*[19] The scope of the technique is shown in a slightly later publication.[20] The technique has been extensively applied in the determination of reaction mechanisms, see for example Grant and Kuwana.[21] So far there have been no applications of these spectroelectrochemical techniques in quantitative analysis, possibly because of the inherent lack of sensitivity of the methods due to the very short path-length containing the absorbing species in the solution which the light-beam actually traverses.

In this paper, a spectroelectrochemical method is described in which a narrow light-beam is passed at grazing incidence across the surface of a smooth platinum electrode. The absorbance is monitored as dilute aqueous metal ion solutions are electrolysed. Preliminary results describing the absorbance phenomena observed have already been reported.[22] Here detailed results and discussion are presented to determine the

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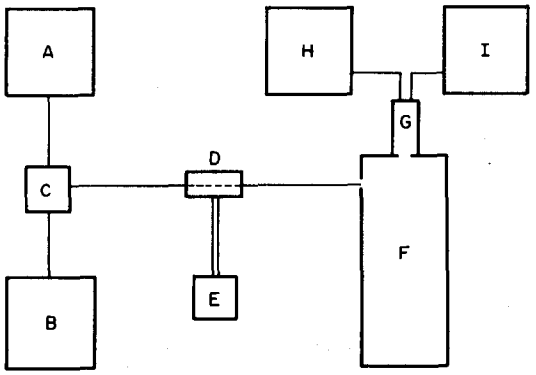

Fig. 1. Schematic diagram of apparatus. A, Power supply for deuterium lamp. B, Power supply for tungsten lamp. C, Lamp housing. D, Cell, E, Potentiostatic waveform source. F, Monochromator. G, PMT. H, EHT supply for PMT. I, Chart recorder.

nature of the electrode process observed and to assess the analytical potential of the method.

EXPERIMENTAL

Apparatus

Spectrophotometer. A simple ultraviolet/visible apparatus (see Fig. 1) was built from the following components: a deuterium lamp (Cathodeon type C70-2V-S) with Unicam SP500 lamp supply, a tungsten filament lamp run from a regulated power supply (APT Electronic Industries type TCU 550), a monochromator (Optika CE4), a photomultiplier (EMI type 6256B) with power supply (Brandenburg type 475R), a chart recorder (Smith's Industries Servoscribe type RE11.20).

Cell assembly. This is shown in Fig. 2. A 2-cm silica cell was used, containing two polished platinum plate electrodes. The cell was fitted with an inlet for oxygen-free nitrogen, an outlet for removal of solutions by suction and an agar/KCl salt bridge to a saturated calomel reference electrode (SCE). The cell assembly was mounted on vertical and horizontal racking movements, in turn mounted on an optical bar (Ealing Tri-rack). Fixed horizontal slits were mounted on either side of the cell. Vertical movement of the cell ensured that the light-beam was of a suitable height (approx. 0.5 mm) whereas lateral movement ensured that light passed only over the electrode surface.

Potential source. A potentiostatic waveform source was used (Chemtrix type 804). This provided ramp or step functions in either a two-or three-electrode mode of operation.

Reagents

Stock 1% metal ion solutions were prepared by dissolving the appropriate amount of the analytical-reagent grade salt (usually chloride or sulphate) in 100 ml of distilled water. A stock (0.3 *M*) background electrolyte solution was prepared by dissolving the appropriate amount of analytical grade potassium sulphate in 1 litre of distilled water. Working solutions of typically 10 ppm metal in 0.03 *M* potassium sulphate were prepared daily by dilution.

Procedure

The function generator was preset so that when it was switched on a constant potential was applied to the electrode in the light-path (the working electrode) so that this electrode became the cathode. A 5-ml aliquot of the working solution, the bulk of which was continuously deaerated with oxygen-free nitrogen, was transferred to the cell and deaerated further for 60 sec. The solution was kept under a nitrogen blanket throughout. The gain of the system was adjusted so that at the required wavelength a setting of 0% absorption was obtained on the chart recorder, with 100% absorption being obtained when the light-beam was interrupted by a piece of opaque material. The chart recorder was started and the function generator switched on to its preset value, then the absorption signal was recorded until a maximum was reached (typically 30 sec). The solution was removed from the cell by suction and the working electrode cleaned by application of a high positive potential while the electrode was rinsed with background electrolyte solution. Potentials of up to 5.0 V with respect to the counter-electrode were used. The electrodes were finally rinsed with distilled water.

RESULTS

By use of the procedure above, the variation of absorbance with a number of experimental parameters was investigated for several metal ion solutions.

Potential difference

For those metals which gave rise to an absorbance signal, the results obtained were essentially similar. The results for cobalt are shown in Fig. 3, and the results for the other metals in Table 1.

Wavelength

The absorption spectra obtained are shown in Fig. 4 and the wavelengths of the absorption maxima are given in Table 1. These spectra are corrected for the absorbance obtained with the background electrolyte alone. This spectrum is shown in Fig. 5.

Concentration

At a suitable potential and wavelength the analyti-

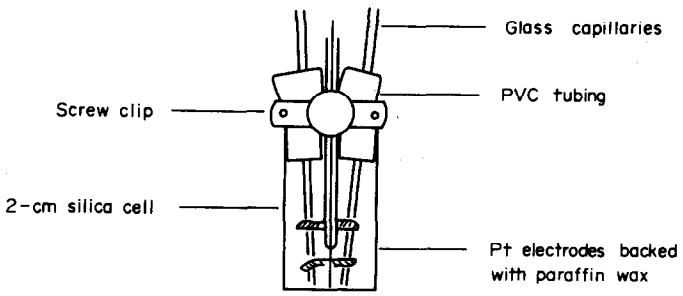

Fig. 2. Cell and electrode assembly.

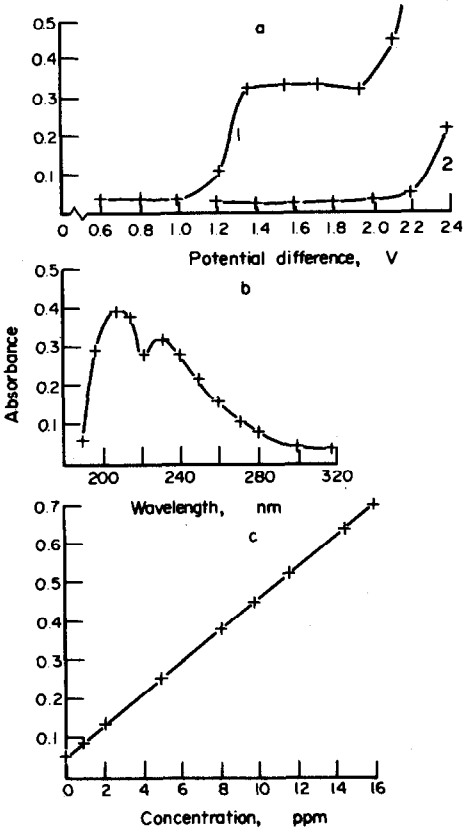

Fig. 3. Variation of absorbance with (a) potential difference, curve 1, 10 ppm cobalt at 225 nm; curve 2, blank solution: (b) wavelength (10 ppm and 1.4 V): (c) concentration (210 nm, and 2.0 V).

cal growth curve for each metal was obtained. The linear region of the calibration curve and the sensitivity (concentration for 1% absorption) are given in Table 1.

Distance from the electrode surface and time

The variation of the absorbance with time as the electrode was moved progressively out of the light-beam is shown in Fig. 6. The solution used was 10 ppm cobalt. This type of relationship was shown by all the metals.

Pretreatment of the electrode

It is well known that a platinum electrode is not electrochemically inert[23] and various potential regions corresponding to hydrogen adsorption and desorption, oxide formation and oxide reduction can be identified.[24] It is apparent that the conditions used to clean the electrode surface by anodic stripping in the procedure would have left the electrode surface coated with a layer of platinum oxide.

The effect of the pretreatment on the absorbance for 20 ppm zinc (at 205 nm) and for the background electrolyte alone (at 198 nm) is shown in Table 2. The effect of the nature of the electrode surface at the start of the electrolysis is shown in Fig. 7a, b, for 20 ppm cadmium and 0.03 *M* potassium sulphate. In these experiments the first stage of the procedure was modified so that a linearly decreasing potential (with respect to the SCE) was applied to the working electrode. The potential sweep-rate used was 50 mV/sec.

Initial pH of the solution

The effect of increasing the sulphuric acid concentration of the solution was studied for 10 ppm cadmium and 0.03*M* potassium sulphate. The results are shown in Table 3. All the absorbances were measured at a potential of −0.2 V *vs.* the SCE.

Change in pH near the electrode

It is known that during electrolysis at inert electrodes the solution near the cathode becomes alkaline when hydrogen is evolved.[25] The effect has been subjected to theoretical analysis.[26–28] To follow any changes in pH near the working electrode a 10^{-3}% solution of phenolphthalein in 0.03*M* potassium sulphate was used. The absorbance at 552 nm was followed, this being the absorbance maximum of the alkaline form of the indicator. The absorbance as a function of potential (linear sweep-rate 50 mV/sec) is shown in Fig. 7c for an oxidized and a reduced electrode surface.

Spectra of metal ions in alkaline solution

The absorption spectra of the metal ion solutions in 0.03*M* potassium sulphate were recorded (Perkin-

Table 1. Summary of results

Metal	Plateau region of absorbance *vs.* potential variation, *V*	Linear range of calibration curve, *ppm*	Sensitivity, *ppm*	λ_{max} at electrode surface, *nm*	λ_{max} in 10^{-3} *M* KOH, *nm*
Cd	—	0–15	0.09	215	215
Co	1.4–2.0	0–15	0.11	210	212
Cr	1.4–1.8	0–8	0.05	215	205
Cu	1.6–2.0	0–15	0.10	235	237
Fe(II)	—	–	—	270	—
Fe(III)	—	0–10	0.09	270, 364	260, 360
Mn	1.9–2.0	0–12	0.08	210	215
Ni	1.6–2.0	0–20	0.16	208	210
Pb	—	20–50	0.35	270	234
Zn	0.9–1.8	0–12	0.08	207	207

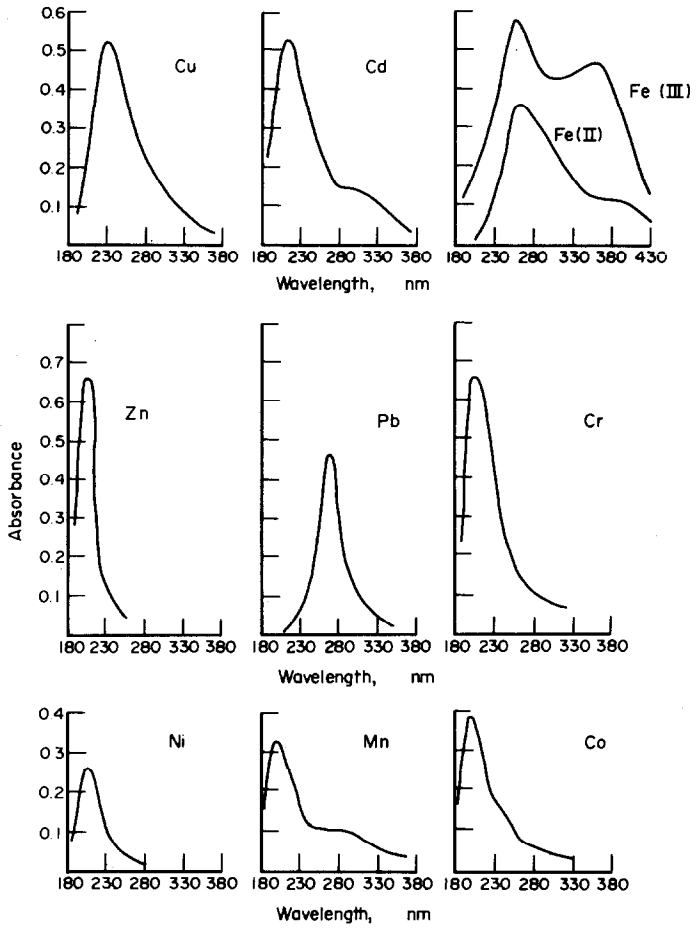

Fig. 4. Absorption spectra of electrogenerated species. All 10 ppm except Fe(II), 5 ppm.

Elmer model 402 ultraviolet/visible spectrophotometer) immediately after the solution was made $10^{-3}M$ with respect to potassium hydroxide. The spectra are shown in Fig. 8. The absorbance maxima are given in Table 1.

DISCUSSION

The results show that undoubtedly the absorbance phenomena observed are due to a reaction or reactions at the electrode surface and that the absorbing product or products then diffuse away from the electrode.

Although the absorbances for the metal ion solutions were found to be independent of the intensity of the incident light-beam, this does not indicate whether the attenuation of the light-beam was by true absorption or Rayleigh scattering (*i.e.*, by particles small in comparison with the wavelength of the inci-

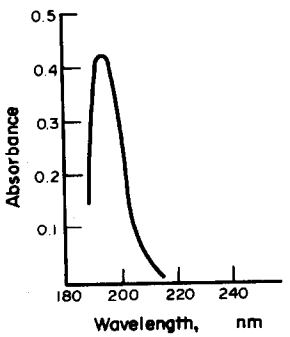

Fig. 5. Absorption spectrum of electrogenerated species from blank solution, $0.03M$ K_2SO_4.

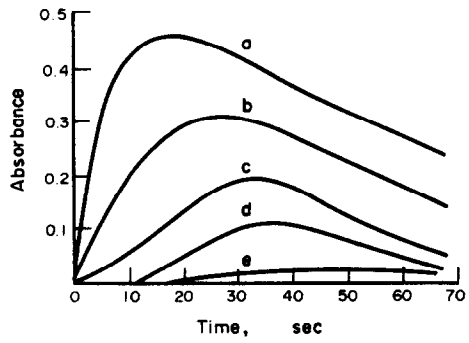

Fig. 6. Variation of absorbance with time for various distances from the electrode surface. (a) 0.05, 0.09, 0.15 and 0.20 mm. (b) 0.80 mm. (c) 1.40 mm. (d) 1.80 mm. (e) 2.20 mm.

Table 2. Effect of pretreatment

Zinc solution		Blank solution	
Pretreatment cycle, V	Max. absorbance at 205 nm and −1.4 V	Pretreatment cycle, V	Max. absorbance at 200 nm and −1.4 V
+2.0, −2.0	0.025	0.0	0.190
+3.0, −3.0	0.029	+1.0	0.036
+3.5, −3.5	0.029	+2.0	0.053
+4.0, −4.0	0.141	+3.0	0.080
+4.0	>1	+4.0	0.152
+5.0	>1	+5.0	0.167
		+5.0, −0.5	0.165
		+5.0, −1.0	0.104
		+5.0, −1.5	0.035
		+5.0, −2.0	0.028

dent light). Both of these phenomena give rise to values of log ϕ_0/ϕ_t (where ϕ_0 is the incident radiant flux and ϕ_t is the transmitted radiant flux) that are independent of ϕ_0. The theory for the scattering of light was developed by Debye[29] who defined the turbidity of a solution, τ, in terms such that $\phi_t/\phi_0 = \exp(-\tau l)$, where l is the path-length in the scattering medium, ϕ_0 is the incident radiant flux and ϕ_t is the transmitted radiant flux, and deduced that, at high dilution, $\tau = Kc/\lambda^4$, where K is a constant, c is the concentration and λ is the wavelength; thus $\ln(\phi_0/\phi_t) = Kcl/\lambda^4$. The Beer–Lambert law for absorption predicts that $\ln(\phi_0/\phi_t) = kcl$, and thus the absorbance, defined as log (ϕ_0/ϕ_t) will be independent of the incident radiant flux whether the light beam is attenuated by true absorption or Rayleigh scattering. The problem of distinguishing between these two phenomena has been discussed as long ago as 1946 by Heller and Vassy,[30] who proposed distinguishing between them on the basis of the value of the wavelength exponent, n, in the equation $k = K\lambda^{-n}$, where k is the absorption coefficient. They deduced that for true absorption n may vary between 0 and $\pm\infty$, whereas for scattering, n may vary between 0 and 4. Furthermore, for true absorption n changes rapidly with wavelength, whereas for scattering n changes only very slightly over spectral ranges of up to 100 nm. The values of n for the spectrum obtained with a 10-ppm cadmium solution (uncorrected for the absorption obtained with the background electrolyte alone) were found by plotting log (absorbance) against log λ, assuming the absorbance to be proportional to the absorption coefficient. The values obtained varied from −23 at 195 nm through 0 at 201 nm to +23 at 275 nm. These values do not rule out the possibility of colloidal material being produced at the electrode, as it is known that colloidal solutions can absorb light according to the Beer–Lambert law.[31]

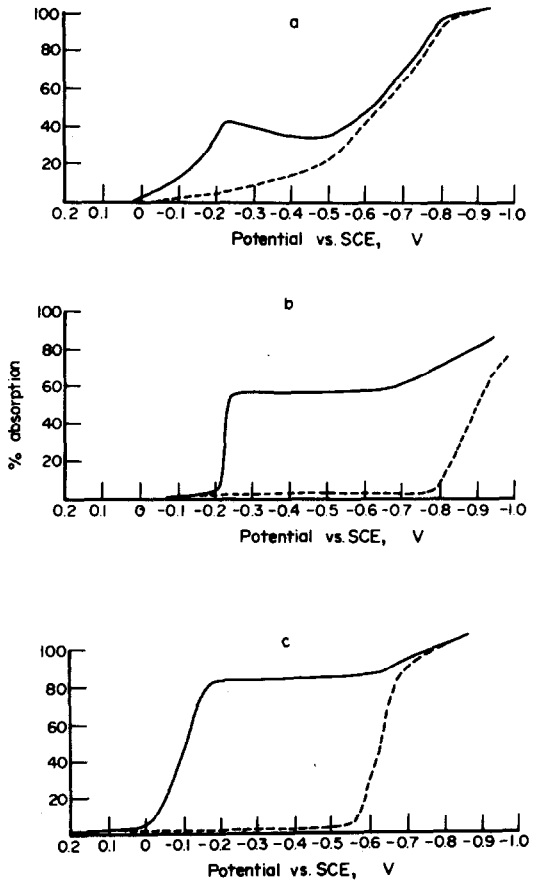

Fig. 7. Variation of % absorption with potential (*vs.* SCE) for (a) blank solution at 198 nm, (b) 20 ppm Cd^{2+} at 215 nm, (c) 0.001% phenolphthalein at 552 nm, Continuous line; oxidized surface, Broken line; oxide-free surface.

It was originally suggested that the absorbing species might be an intermediate in the process of deposition of the metal onto the platinum surface.[32] There are two problems associated with this theory, the first of which is thermodynamic.

The accessible potential range in the system is governed by the potential at which hydrogen gas is evolved from the working electrode, obscuring the light-beam. The sum of the IR drop and oxygen evolution overvoltage was calculated from the potential difference at which hydrogen was observably evolved, and this, in turn, was used to calculate the deposition potential for 10^{-4} M solutions of the metal ions studied. These values are given in Table 4. It can

Table 3. Variation of absorbance with pH

Sulphuric acid conc., *M*	Initial potential, *V vs.* SCE	Final potential, *V vs.* SCE	Cd absorbance, at 220 nm	Blank absorbance at 195 nm
none added	+0.2	−0.2	0.40	0.46
10^{-5}	+0.2	−0.2	0.00	0.36
10^{-4}	+0.2	−0.2	0.00	0.00
10^{-3}	+0.2	−0.2	0.00	0.00
10^{-2}	+0.2	−0.2	0.00	0.00
10^{-5}	+0.6	−0.2	0.41	0.47
10^{-4}	+0.6	−0.2	0.22	0.34
5×10^{-3}	+0.6	−0.2	0.04	0.05
10^{-3}	+0.6	−0.2	0.00	0.00

be seen that a number of metals (Ni, Co, Cd, Fe, Cr, Zn, Mn) would not be deposited within the accessible potential range. However, it has long (if not widely) been known that monolayer or submonolayer amounts of metals are deposited at "underpotentials",[33] *i.e.*, at potentials more anodic than those calculated here. The reason for this is that the full Nernst equation includes a term to account for the activity of the deposit, through energy changes at the electrode–deposit interface.[34,35] The phenomenon has been extensively studied experimentally, initially by the use of the twin-electrode thin-layer cell developed by Schmidt *et al.* (see for example ref. 36) and more recently by the combination of spectroscopic techniques which monitor the nature of the electrode surface (such as ellipsometry and specular reflection spectroscopy) and electrochemical methods (see for example ref. 37). Experimental methods and results have recently been reviewed,[38,39] and it appears that underpotentials of between 0.3 and 0.6 V are observed

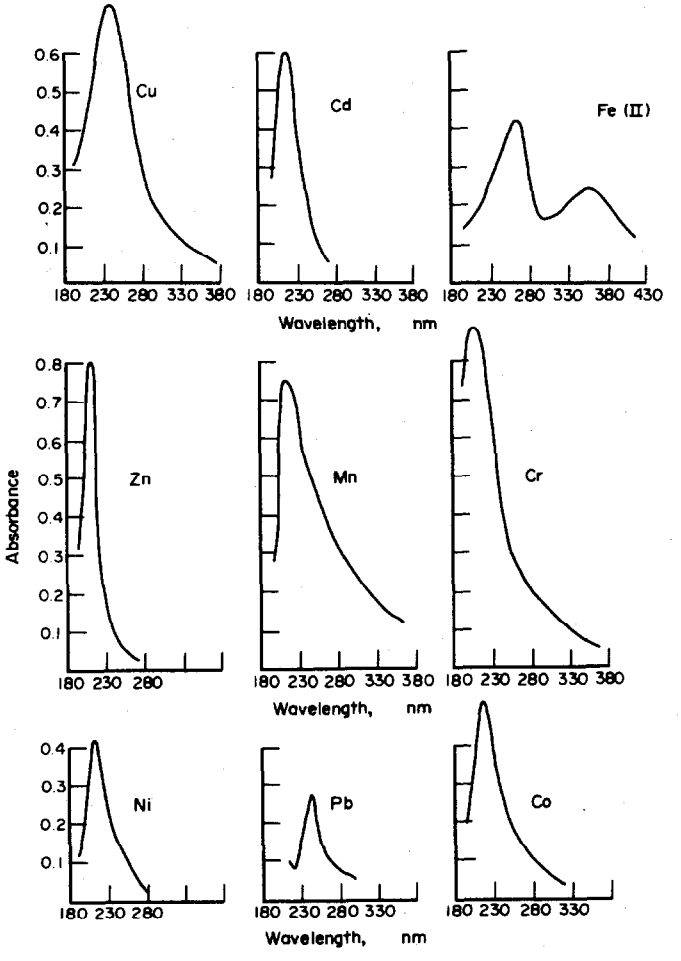

Fig. 8. Absorption spectra of metal ion solutions 10^{-3} M in KOH. Cu, Cd, Zn, Mn, Ni and Co, 10 ppm; Fe(II), Cr, 5 ppm, Pb 20 ppm.

Table 4. Decomposition potentials

Ion discharged	E^0, V	E_{decomp}, V
H^+ (pH 6)	0.00	2.20
Ag^+	0.80	1.16
Hg^{2+}	0.85	1.21
Cu^{2+}	0.34	1.62
Fe^{3+}	−0.04	1.96
Pb^{2+}	−0.13	2.09
Sn^{2+}	−0.14	2.10
Ni^{2+}	−0.25	2.21
Co^{2+}	−0.28	2.24
Cd^{2+}	−0.40	2.36
Fe^{2+}	−0.44	2.40
Cr^{3+}	−0.74	2.76
Zn^{2+}	−0.76	2.72
Mn^{2+}	−1.18	3.24

for electrode materials such as gold, silver and platinum. If the potentials calculated in Table 4 were too large by 0.6 V, then up to a monolayer of the metals could be deposited within the accessible potential range.

The second problem with this theory is mechanistic, namely, at what stage in the reduction process absorbing entities are produced at large distances (in terms of the double-layer thickness) from the cathode surface or with sufficient lifetimes and in sufficient amounts to diffuse away from the electrode surface and interact measurably with the light-beam.

Despite the vast amount that has been written about the deposition of metals from aqueous solutions, it is difficult to discover the mechanism involved as opposed to an analysis of the process from a kinetic viewpoint. At present authors appear to favour a mechanism the initial steps of which are based on the mechanism of hydrogen evolution (which has been well characterized[40]) namely, that after transport to the electrified interface, vibration of the ion within the surrounding water molecules (solvation sheath) produces a condition under which an electron can be transferred from the Fermi level (modified by the application of a cathodic potential) in the electrode to the ion by a process of quantum mechanical tunnelling.[41]

The next stage in the process is not clearly defined. According to Bockris and Damjanovic[42] the partially neutralized hydrated entity is adsorbed onto the electrode surface (they refer to this entity as an adion), which then undergoes a two-dimensional random-walk process accompanied by successive diminution in hydration and successive increase in the number of electrode metal atoms which co-ordinate the particle under consideration, until the ion is eventually incorporated into the electrode crystal lattice. It is not clear how or when the second electron is transferred. Bockris has more recently considered the problem[43] and considers that there is good experimental evidence that mechanisms involving univalent intermediates prevail. This presumably means that the second electron is transferred to a species in solution and that there is the possibility of a homogeneous redox reaction (disproportionation) occurring which would produce neutral hydrated species as well as the original doubly-charged hydrated species.

Recently, the mechanism of charge transfer in the hydrogen evolution reaction has been the subject of some discussion following Walker's presentation of evidence for the involvement of hydrated electrons as precursors in this reaction.[44] The status of solvated electrons in aqueous electrochemical reactions has been examined closely and the pros[45] and cons[46] debated with some vigour, and it is apparent that the question is not yet resolved. If the absorbing species were produced from the reaction between hydrated ions and hydrated electrons then it would be expected that spectra would be similar to those observed when metal ions react with hydrated electrons produced by radiolysis (the usual and original method of production). Such a study was made by Baxendale *et al.*[47] who recorded the ultraviolet/visible spectra of species generated when metal ions (including Cu^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+}, Ag^+) reacted with hydrated electrons produced by a 2-μsec pulse of 4-MeV electrons from a linear accelerator. They found that all the spectra of the transient species produced were similar with an absorbance maximum at around 310 nm.

None of these mechanisms for the production of the absorbing species as an intermediate in the electrodeposition reaction accounts for the involvement of the electrode surface observed here and the considerable effect that the nature of the surface has on the magnitude of the signals. As was indicated earlier, the surface of the platinum could be either oxidized or reduced (oxide-free). The anodic film on platinum has been extensively studied by a wide variety of experimental techniques including spectroelectrochemical methods[3] and the literature has been comprehensively reviewed.[48–50] Although there is still some doubt over the nature of the film (which in any case varies with the potential) it may be considered that, under the conditions employed here, the surface of the oxidized electrode would be covered with platinum oxide phases rather than adsorbed oxygen species. What is of greater interest is the mechanism of reduction of this oxide layer and the products of the reduction, *i.e.*, what happens to the surface when a cathodic potential is applied. Despite the many different formulations of the oxide phases, it appears to be generally accepted that in acid solution the final stage in the reduction is

$$PtOH + H^+ + e^- \rightarrow Pt + H_2O$$

(see for example refs. 49, 51).

The results of the experiments with phenolphthalein solution indicate that in the potential region in which the surface oxide is reduced, *i.e.*, between 0.0 and −0.2 V *vs.* SCE, (see Fig. 7) the solution near the electrode becomes alkaline when an oxidized elec-

trode surface is used. If a reduced electrode surface is used then no hydroxide ion is produced in this potential region. It is proposed that the absorbance obtained with the background electrolyte alone is due to OH^-. Confirmation was obtained by comparing the absorption spectrum (Fig. 5) with that of a solution of potassium hydroxide. What also emerges from Fig. 7 is that at more negative potentials (from about -0.5 to -0.6 V) there is another process producing OH^- near the electrode. Hydrogen evolution did not obscure the light-beam until the potential was greater than -0.8 V. It is suggested that this is the first stage in the reduction of water to hydrogen, which is adsorbed by the platinum electrode and thus does not obscure the light-beam, and hydroxyl ion.

It is clear from the results that the absorption of light observed when the metal ion solutions are electrolysed is connected directly with the production of an alkaline layer next to the cathode surface. This is shown by Fig. 7 and from the fact that when the solution is made increasingly acid, thus reducing the thickness of the alkaline layer, the observed absorbance decreases and eventually disappears altogether (Table 3). The absorption spectra obtained on adding potassium hydroxide to the metal ion solutions (Fig. 8) are very similar to those obtained at the electrode surface (Fig. 4). Thus it is concluded that the absorbance is due to the production of hydroxo-complexes adjacent to the cathode, following the production of hydroxyl ions. The overall mechanism proposed is:

1. Reduction of the surface oxide layer to give OH^- in solution near the cathode.
2. OH^- diffuses into the solution under the concentration gradient.
3. Metal ions in the solution react rapidly to form the hydroxo-complexes which give rise to the absorbances measured.
4. As the surface oxide is removed the production of OH^- decreases and eventually ceases.
5. Correspondingly, the absorbance decreases as the hydroxo-complexes dissociate, and diffuse out of the light-path.

That this increase in alkalinity of the catholyte has not been reported more often in the literature is attributed to the fact that most electrochemical studies are made in fairly acid or fairly alkaline solutions. In neither of these solutions would the phenomenon be observed.

Analytical applications

In effect, the technique developed is a solution spectrophotometric method using electrogenerated hydroxyl ions as a general spectrophotometric reagent. Hydroxide ion has not found use as a spectrophotometric reagent for two reasons; first the absorption of the resulting metal hydroxo-complex lies in the ultraviolet and secondly, and more important, with many metals an insoluble hydroxide precipitates, which would give rise to extremely poor precision. However, under the conditions employed here, the formation of the complex is controlled by the dynamic conditions in the diffusion layer next to the cathode and good reproducibility is obtained. The values for the molar absorptivities of the hydroxo-complexes are similar to those for the metal complexes of other general colorimetric reagents such as 8-hydroxyquinoline and diethyldithiocarbamate. The method is applicable only to those metals which form absorbing hydroxo-complexes, but is not restricted to those reducible in the potential range accessible and has the advantages that addition of external reagents, waiting for the colour to develop, *etc.* are not necessary. Control of the potential of the working electrode controls the pH in the diffusion layer to a certain extent but is unlikely to offer much in the way of introducing selectivity to the method. It would seem feasible to apply the method to the detection of metal ions following separation, for example by chromatography. Recently the ultraviolet monitoring of metal chloride complexes has been suggested as a method of detection in chromatography.[52] Use of a suitably designed cell and electrogenerated hydroxide would offer advantages of selectivity and sensitivity over the use of chloride.

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CATALYTIC EFFECT OF COPPER ON THE HEXACYANOFERRATE(III)–CYANIDE REDOX REACTION—I

THE UNCATALYSED AND CATALYSED REACTIONS

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Summary—A kinetic study of the hexacyanoferrate(III)–cyanide redox reaction has been made in connection with development of a new catalytic method for copper. The reaction kinetics change with time from first- to second-order dependence with respect to hexacyanoferrate(III). The reaction is nearly inverse first-order with respect to hexacyanoferrate(II) and first-order with respect to cyanide. The reaction shows a strong positive primary salt effect, but a very small increase in the reaction rate with temperature is found. A parallel reaction proceeds with a first-order dependence with respect to hydroxide. A tentative mechanism is proposed for the first reaction, involving the formation of cyanogen radicals. The second reaction corresponds to the well-known decomposition of hexacyanoferrate(III) in alkaline medium. The catalysed reaction exhibits similar kinetics with respect to hexacyanoferrate(II) and (III) but is zero-order with respect to cyanide and hydroxide and first-order with respect to catalyst. The proposed mechanism involves two consecutive interactions of the hexacyanoferrate(III) with copper(I) and with copper(II) cyanide complexes respectively, followed by a 2-electron oxidation of a co-ordinatively bridging cyanide group.

Kinetic methods of analysis have undergone wide development in the last few years. Those based on catalytic reactions are especially sensitive and therefore applied to inorganic trace analysis. Most of the published papers deal only with the strictly analytical applications, but knowledge of the kinetics and mechanisms of the uncatalysed and catalysed reactions can be very useful for optimizing the experimental conditions to achieve the lowest detection limit.

Hexacyanoferrate(III) has useful oxidizing properties in both acidic and alkaline media because the standard potential of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox system is practically unaffected by change in pH:

$$Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-} \qquad E_0 = 0.36\,V$$

On the other hand, cyanide can be oxidized to cyanogen or to cyanate, depending on the pH, as can be deduced from the potentials:[1]

$$\tfrac{1}{2}(CN)_2 + H^+ + e \rightleftharpoons HCN \qquad E_0 = 0.37\,V$$

$$CNO^- + 2H^+ + 2e \rightleftharpoons CN^- + H_2O \qquad E_0 = 0.14\,V$$

The redox reaction between hexacyanoferrate(III) and cyanide in alkaline medium is thermodynamically favourable, but this reaction is slow.[2–4] The only kinetic investigation of this reaction is due to Adamson,[2] who found an apparent reaction order between first and second, a retarding effect by hexacyanoferrate(II), a dependence between first- and second-order on total cyanide concentration and a small, possibly negative, temperature coefficient.

We have found that the reaction is strongly catalysed by copper and a previous communication was published containing the first kinetic results.[5]

In this paper a kinetic study of the hexacyanoferrate(III)–cyanide redox reaction with and without added copper is reported, and a tentative mechanism for the reactions is proposed. Part II[5a] will describe the analytical application of the catalysed reaction.

EXPERIMENTAL

Reagents

Solutions of hexacyanoferrate(III) and hexacyanoferrate(II) were made from the required amounts of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6 . 3H_2O$. Solutions of sodium cyanide were standardized by the Liebig–Denigès method. Sodium hydroxide solutions were standardized against potassium hydrogen phthalate. Copper(II) solutions were prepared from $Cu(NO_3)_2 . 3H_2O$ and standardized iodometrically. To adjust the ionic strength, sodium chloride (solid or concentrated solution) was used. Analytical-reagent grade chemicals were used throughout.

Apparatus and procedure

The reaction rate was followed spectrophotometrically by measuring the change in absorbance of the hexacyanoferrate(III) solutions at 422 nm, by using a Beckman DB-GT spectrophotometer with a coupled Beckman recorder. At this wavelength the other species in solution do not interfere. Solutions were prepared in a 50-ml standard flask by adding the required amounts of sodium cyanide solution, copper solution for the catalysed-reaction and analytical studies, sodium chloride to adjust the ionic strength, sodium hydroxide solution, and potassium hexacyanoferrate(II) solution. All the solutions were previously

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heated to working temperature in a thermostat. The resulting solution was diluted to nearly 40 ml and kept in the thermostatic bath for 30 min. Then 5 ml of potassium hexacyanoferrate(III) solution were added with stirring and the volume was quickly adjusted to 50 ml. The solution was transferred to the spectrophotometric cell and the kinetic curve was recorded with zero time taken as the moment at which the hexacyanoferrate(III) solution was added.

The temperature in the cell was kept constant within ±0.2° during each experiment.

RESULTS AND DISCUSSION

The uncatalysed reaction

Stoichiometry. Different excesses of $Fe(CN)_6^{3-}$ relative to NaCN were added and the equilibrium amounts of $Fe(CN)_6^{3-}$ remaining were determined spectrophotometrically. The hexacyanoferrate(III) and cyanide consumed were found to be in 2:1 molar ratio. Therefore the stoichiometry of the reaction will be, in agreement with other workers:

$$2Fe(CN)_6^{3-} + CN^- + 2OH^- \longrightarrow 2Fe(CN)_6^{4-} + CNO^- + H_2O \quad (1)$$

Effect of hexacyanoferrate(III) concentration. A plot of the logarithm of the initial rate (first 2–3 min) *vs.* log $[Fe(CN)_6^{3-}]$ is linear, showing a first-order dependence on the hexacyanoferrate(III) concentration in the absence of hexacyanoferrate(II). However, plots of log *A vs.* time (Fig. 1) show that the dependence is first-order only at the start of the reaction [the plots are not straight lines but the initial slopes are independent of hexacyanoferrate(III) concentration and have the same value as that obtained by the initial-rate method, as can be seen in Table 1]. It was also found that after an initial period of about 20 min the second-order plots of $1/A$ against time were straight lines (Fig. 2). The slopes of the straight lines decrease as the hexacyanoferrate(III) initial concentration increases, showing an inhibiting effect which could be due to hexacyanoferrate(III) itself, the hexacyanoferrate(II) produced or perhaps both species simultaneously.

Table 1. Values of the experimental pseudo first-order constant for different initial hexacyanoferrate(III) concentrations

$[Fe(CN)_6^{3-}]$, $M \times 10^4$	$k_{(1)}$, $min^{-1} \times 10^2$
1	4.9
3	5.6
5	4.6
7	4.8
10	4.5

(NaCN, 1.0*M*; NaOH, 0.1*M*; *I*, 2.0; *T*, 25°C)

Effect of hexacyanoferrate(II) concentration. Hexacyanoferrate(II) shows an inhibiting effect in both the initial rate and the pseudo second-order constant. A plot of initial rates against $[Fe(CN)_6^{4-}]^{-1}$ gives a line that is straight at high $Fe(CN)_6^{4-}$ concentrations, with a positive intercept, showing a reaction with a nearly first-order inverse dependence on hexacyanoferrate(II) concentration (Fig. 3) and a parallel reaction with kinetics not influenced by this species. From the

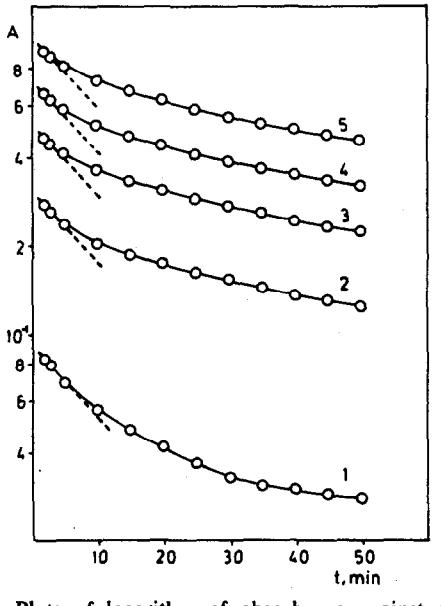

Fig. 1. Plots of logarithm of absorbance against time. NaCN, 1.0*M*; NaOH, 0.1*M*; *I*, 2.0; *T*, 25°C. Curve (1), $K_3Fe(CN)_6$ $1.0 \times 10^{-4}M$; (2), $3.0 \times 10^{-4}M$; (3), $5.0 \times 10^{-4}M$; (4), $7.0 \times 10^{-4}M$; (5), $10 \times 10^{-4}M$.

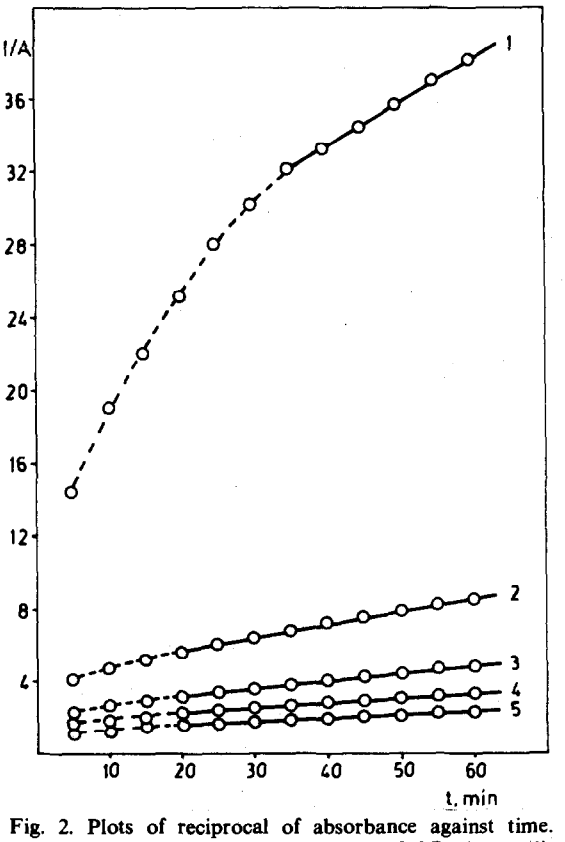

Fig. 2. Plots of reciprocal of absorbance against time. NaCN, 1.0*M*; NaOH, 0.1*M*; *I*, 2.0; *T*, 25°C. Curve (1), $K_3Fe(CN)_6$ $1.0 \times 10^{-4}M$; (2), $3.0 \times 10^{-4}M$; (3), $5.0 \times 10^{-4}M$; (4), $7.0 \times 10^{-4}M$; (5), $10 \times 10^{-4}M$.

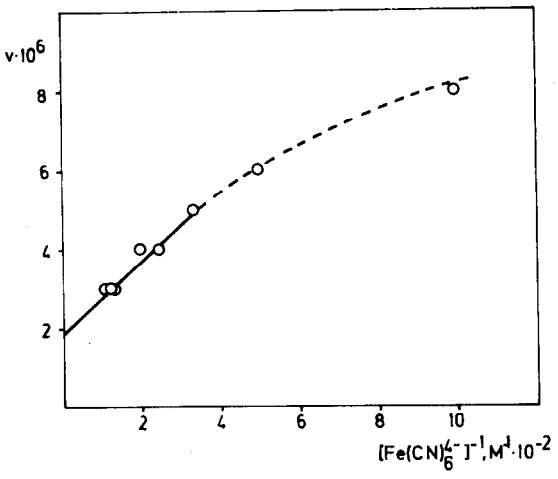

Fig. 3. Plot of initial rate against the reciprocal of hexacyanoferrate(II) concentration. $K_3Fe(CN)_6$, $5 \times 10^{-4}M$; NaCN, $1.0M$; NaOH, $0.1M$; I, 2.0; T, 25°C.

curvature of the line at low $Fe(CN)_6^{4-}$ concentrations some additional inhibiting effect of $Fe(CN)_6^{3-}$ can be deduced. The most adequate representation of the experimental pseudo second-order constant is a plot of k_{exp} against $([Fe(CN)_6^{3-}] + [Fe(CN_6^{4-}])^{-1}$ which also includes the possible inhibiting effect of the $Fe(CN)_6^{3-}$. A straight line with positive intercept is obtained, which confirms the existence of two parallel paths for the reaction.

Effect of cyanide concentration. Plots of initial rates or experimental pseudo second-order constants against cyanide concentration give straight lines with positive intercepts. This again suggests that the $Fe(CN)_6^{3-}$ is involved in two parallel reactions, one first-order and the other zero-order with respect to cyanide concentration.

Effect of sodium hydroxide concentration. A straight line with a low slope and a large intercept was obtained on plotting initial rates or k_{exp} against $[OH^-]$. The intercepts in the plots of k_{exp} *vs.* $([Fe(CN)_6^{3-}] + [Fe(CN)_6^{4-}])^{-1}$ and *vs.* $[CN^-]$ are of the same order while that for k_{exp} *vs.* $[OH^-]$ is about ten times as great. This suggests that the results obtained can be described by an equation of the type:

$$k_{exp} = \frac{k[CN^-]}{[Fe(CN)_6^{3-}] + [Fe(CN)_6^{4-}]} + k'[OH]^- \quad (2)$$

Since k_{exp} seems to be a pseudo second-order rate constant, the differential rate equation can be written as:

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k_{exp}[Fe(CN)_6^{3-}]^2 = \frac{k[CN^-][Fe(CN)_6^{3-}]^2}{[Fe(CN)_6^{3-}] + [Fe(CN)_6^{4-}]} + k'[OH^-][Fe(CN)_6^{3-}]^2 \quad (3)$$

Effect of ionic strength. A positive primary salt effect was found for the reaction. Plotting log k_{exp} *vs.* $I^{\frac{1}{2}}$ according to the Brønsted–Bjerrum equation[6] gave a slope of about +3, which suggests that the activated-complex formation step is a reaction between two ions with charges of the same sign and absolute values 1 and 3.

Effect of temperature. The reaction rate increases very slightly with temperature over the range from 12 to 50°. From an Arrhenius plot of log k_{exp} *vs.* 1/T an activation energy of *ca.* 0.6 kcal/mole was obtained. This value is anomalously low for reactions in solution, and suggests an exothermic reaction preceding the rate-determining step. This experimental value is therefore probably an apparent activation energy which is lower than the true one. The activation enthalpy and entropy obtained are close to zero and -59 cal.mole^{-1}.deg^{-1} respectively.

Mechanism of reaction. According to equation (3) hexacyanoferrate(III) is involved (with a pseudo second-order dependence) in two parallel reactions: one of them is first-order with respect to CN^-, negative order to $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, and zero-order to OH^-, while the other is first-order with respect to OH^- and independent of the CN^- and $Fe(CN)_6^{4-}$ concentrations.

The first reaction probably takes place by interaction of hexacyanoferrate(III) and cyanide ions through a mechanism which essentially consists of the following steps:

$$Fe(CN)_6^{3-} + CN^- \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} Fe(CN)_6^{4-} + CN^\cdot \quad (4)$$

$$Fe(CN)_6^{3-} + CN^\cdot \xrightarrow{k_b} Fe(CN)_6^{4-} + CN^+ \quad (5)$$

$$CN^+ + 2OH^- \xrightarrow{fast} CNO^- + H_2O \quad (6)$$

If reaction (5) is sufficiently faster than the reverse of reaction (4) the actual concentration of cyanogen radical will be small. If the steady-state treatment is applied to this species, the following equation can be deduced:

$$v = -\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{2k_a k_b[CN^-][Fe(CN)_6^{3-}]^2}{k_{-a}[Fe(CN)_6^{4-}] + k_b[Fe(CN)_6^{3-}]}$$

From the experimental data it can be deduced that $k_{-a} \simeq k_b$ and therefore the rate equation can be simplified to:

$$v = \frac{2k_a[CN^-][Fe(CN)_6^{3-}]^2}{[Fe(CN)_6^{4-}] + [Fe(CN)_6^{3-}]} \quad (8)$$

and the pseudo second-order constant will be:

$$\frac{2k_a[CN^-]}{[Fe(CN)_6^{4-}] + [Fe(CN)_6^{3-}]} \quad (9)$$

However, in the initial stages and in the absence of $Fe(CN)_6^{4-}$, since $[Fe(CN)_6^{4-}] \ll [Fe(CN)_6^{3-}]$, the rate will assume the form $v = 2k_a[CN^-][Fe(CN)_6^{3-}]$, an equation with a first-order dependence on $Fe(CN)_6^{3-}$ and where the pseudo first-order constant is $k_1 = 2k_a[CN^-]$, in good agreement with the experimental results.

Table 2. Values of the calculated and experimental pseudo second-order rate constants ($l.\ mole^{-1}.min^{-1}$) for different conditions

(1)			(2)			(3)			(4)		
$[Fe(CN)_6^{3-}]_0$, $M \times 10^4$	k_{cal}	k_{exp}	$[Fe(CN)_6^{4-}]_0$, $M \times 10^3$	k_{cal}	k_{exp}	$[CN^-]$, M	k_{cal}	k_{exp}	$[OH^-]$, M	k_{cal}	k_{exp}
1.0	114*	187	1.0	17*	15	0.2	9	11	0.02	32	32
3.0	48	56	2.0	10*	10	0.4	14	15	0.04	33	33
5.0	33	34	4.0	7*	6	0.6	20	22	0.1	34	37
7.0	25	27	5.0	6*	5	0.8	27	26	0.2	36	44
10.0	19	17	8.0	4*	5	1.0	33	39	0.4	40	51
						1.2	39	40	0.6	45	61
						1.4	45	49	0.8	49	69
						1.6	51	53			
						1.8	57	60			

* Calculated from the equilibrium state.
(1) Effect of hexacyanoferrate(III) concentration. $K_4Fe(CN)_6$, $10^{-4}M$; NaCN, $1.0M$; NaOH, $0.1M$; I, 2.0; T, 25°C.
(2) Effect of hexacyanoferrate(II) concentration. $K_3Fe(CN)_6$, $5.0 \times 10^{-4}M$; NaCN, $1.0M$; NaOH, $0.1M$, 2.0; T, 25°C.
(3) Effect of cyanide concentration. $K_3Fe(CN)_6$, $5.0 \times 10^{-4}M$; $K_4Fe(CN)_6$, $10^{-4}M$; NaOH, $0.1M$; I, 2.0; T, 25°C.
(4) Effect of hydroxide concentration. $K_3Fe(CN)_6$, $5.0 \times 10^{-4}M$; $K_4Fe(CN)_6$, $10^{-4}M$: NaCN, $1.0M$; I, 2.0; T, 25°C.

If the OH^- effect [equation (2)] is included, the experimental rate will have the form:

$$v_{exp} = \frac{2k_a[CN^-][Fe(CN)_6^{3-}]^2}{[Fe(CN)_6^{4-}] + [Fe(CN)_6^{3-}]} + k'[OH^-][Fe(CN)_6^{3-}]^2 \quad (10)$$

and the pseudo second-order rate constant will be

$$k_{exp} = \frac{2k_a[CN^-]}{[Fe(CN)_6^{4-}] + [Fe(CN)_6^{3-}]} + k'[OH^-] \quad (11)$$

From the slope and intercept of the plot of k_{exp} *vs.* $([Fe(CN)_6^{3-}] + [Fe(CN)_6^{4-}])^{-1}$, $k_a = \frac{1}{2}k = 9.2 \times 10^{-3}$ $l.mole^{-1}.min^{-1}$ and $k' = 21\ l^2.mole^{-2}.min^{-1}$ were obtained. The k' value obtained from the slope of the straight line plot of k_{exp} *vs.* $[OH^-]$ is larger than this, and this effect is ascribed to copper present as impurity in the sodium hydroxide. The pseudo second-order rate constant was calculated from these results, and gave good agreement with the experimental values, provided that $[Fe(CN)_6^{3-}] \gg [Fe(CN)_6^{4-}]$ (Table 2). Disagreement was observed between the k_{calc} and k_{exp} values at low $[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}]$ ratio, probably because the reaction (5) is too slow in these conditions and the steady-state treatment cannot be applied. The equilibrium state must then be applied to reaction (4), the rate equation then being

$$v = \frac{2k_a[CN^-][Fe(CN)_6^{3-}]^2}{[Fe(CN)_6^{4-}]} \quad (12)$$

or, including the $[OH^-]$ effect,

$$v_{exp} = \frac{2k_a[CN^-][Fe(CN)_6^{3-}]^2}{[Fe(CN)_6^{4-}]} + k'[OH^-][Fe(CN)_6^{3-}]^2 \quad (13)$$

From this, the pseudo second-order rate constant will be:

$$k_{exp} = \frac{2k_a[CN^-]}{[Fe(CN)_6^{4-}]} + k'[OH^-] \quad (14)$$

The values calculated from this equation agree with the experimental ones obtained at low $[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}]$ ratio (Table 2).

At high sodium hydroxide concentration the experimental values were somewhat higher than calculated, this difference being proportional to the alkali concentration. This effect is probably due to the copper impurity already mentioned.

According to the proposed mechanism the reaction is first-order with respect to hexacyanoferrate(III), although a second-order dependence is found experimentally for most of the reaction time. Many other oxidation reactions with $Fe(CN)_6^{3-}$ are known in which complex mechanisms can show apparent second-order kinetics.[7–10] According to Bridgart *et al.*[10] the linearity found by plotting $[Fe(CN)_6^{3-}]$ *vs.* time does not necessarily imply second-order kinetics and the experimental value obtained for the proportionality constant from the slope is not a true rate constant but a parameter which they express by k''.

The second reaction consists, apparently, of an internal electron transfer from the co-ordinated cyanide to the iron(III) in hexacyanoferrate(III). This reaction can be identified with the well-known decomposition of hexacyanoferrate(III) solutions in alkaline medium. In this reaction both the stoichiometry and mechanism are probably complex. The behaviour of $Fe(CN)_6^{3-}$ in alkaline solutions is strongly affected by light and the products of this reaction are not well identified. According to Schwarz and Tede[11] ferric hydroxide and cyanide are the primary products, the cyanide being subsequently oxidized to cyanogen by the unreacted hexacyanoferrate(III). The possibility of formation of aquo-complexes is also considered. Alich

et al.[4] suppose that, in strongly alkaline solution, the OH^- ion is involved in the reduction of hexacyanoferrate(III) by cyanide through an intermediate aquo-complex. According to these considerations we can postulate that the hydrolytic decomposition of $Fe(CN)_6^{3-}$ is only an initiation step which induces a later redox reaction.

The catalysed reaction

The stoichiometry was found to be the same as that for the uncatalysed reaction, and so was the effect of the hexacyanoferrate(III) and hexacyanoferrate(II) concentrations. The kinetics of the catalysed reaction proved to be independent of the cyanide concentration for both the initial rate and pseudo second-order constant (Table 3). The sodium hydroxide concentration had no effect on either the initial-rate or pseudo second-order constant (Table 4), which suggests that only the $Fe(CN)_6^{3-}$–CN^- reaction is catalysed by copper, and that copper does not affect the alkaline decomposition of hexacyanoferrate(III).

There is again a strong positive primary salt effect, showing that the activated complex is formed between two ions with charges of the same sign.

The effect of temperature is greater than for the uncatalysed reaction. From the Arrhenius plot an activation energy of 1.6 kcal/mole was deduced. This is larger than that for the uncatalysed reaction probably because of the anomalously low value of the latter. The enthalpy and entropy of activation were calculated to be 1.0 kcal/mole and -55 cal.mole^{-1}.deg^{-1}.

Effect of copper concentration. The initial reaction rate and pseudo second-order rate constant increase proportionally to the total copper concentration, showing a first-order dependence on the catalyst. The proportionality constant decreases for relatively high concentrations of copper. This is probably due to the inhibiting effect of the larger concentration of hexacyanoferrate(II) produced.

Mechanism of reaction. Copper(II) is readily reduced by the cyanide in the reaction medium and the copper(I) forms stable cyanide complexes. Information about which Cu(I) complex species predominates in cyanide medium is rather scarce. A value of 55 is reported by Baxendale and Wescott[12] for the equilibrium constant between the 1:3 and 1:4 copper(I)–cyanide complexes. From this result we deduce that the $Cu(CN)_4^{3-}$ ion predominates under our experimental conditions. More recently Parkash and Zýka[13] found, by potentiometric titration, that $Cu(CN)_4^{3-}$ is formed in the reaction between Cu^{2+} and CN^- when the $CN^-:Cu^{2+}$ ratio is 5:1. The equilibrium Cu(II) species is essentially the $Cu(CN)_4^{2-}$ complex, according to several authors.[14–17]

Table 3. Values of the initial rates and pseudo second-order constants for different sodium cyanide concentrations

$[CN^-]$, M	$v^c \times 10^6$, $mole.l^{-1}.min^{-1}$	k^c_{exp}, $l.mole^{-1}.min^{-1}$
0.2	9	71
0.6	8	73
1.0	9	72
1.4	8	74
1.8	8	80

($K_3Fe(CN)_6$, $5.0 \times 10^{-4}M$; $K_4Fe(CN)_6$, $10^{-4}M$; NaOH, $0.1M$; $Cu(NO_3)_2$, $4.0 \times 10^{-6}M$; I, 2.0; T, 25°C)

Table 4. Values of the initial rates and pseudo second-order constants for different sodium hydroxide concentrations

$[OH^-]$ M	$v^c \times 10^6$ $mole.l^{-1}.min^{-1}$	k^c_{exp}, $l.mole^{-1}.min^{-1}$
0.04	11	69
0.20	11	67
0.40	11	69
0.60	10	69
0.80	11	70

($K_3Fe(CN)_6$, $5.0 \times 10^{-4}M$; $K_4Fe(CN)_6$, $10^{-4}M$; NaCN, $1.0M$; $Cu(NO_3)_2$, $4.0 \times 10^{-6}M$; I, 2.0; T, 25°C)

The catalytic effect of copper on the hexacyanoferrate(III)–cyanide redox reaction must evidently take place through the Cu(I) $\rightleftharpoons$ Cu(II) catalytic cycle, probably by an initial interaction of hexacyanoferrate(III) and the Cu(I) cyanide complex followed by a rapid oxidation of cyanide by copper(II).

A mechanism can be proposed which agrees with the experimental orders found for hexacyanoferrate (III), hexacyanoferrate(II) and copper and the zero orders for cyanide and hydroxide ion. The first step consists of a non-equilibrium interaction between $Fe(CN)_6^{3-}$ and $Cu(CN)_4^{3-}$:

$$Fe(CN)_6^{3-} + Cu(CN)_4^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(CN)_6^{4-} + Cu(CN)_4^{2-} \quad (15)$$

As is well known, the Cu(II) cyanide complex is unstable and readily decomposes. The mechanism of this reaction has not been well explained but there is no doubt that cyanide is oxidized to cyanogen.[12–15] However, in the copper-catalysed hexacyanoferrate (III)–cyanide reaction, cyanate was virtually the only product of cyanide oxidation. According to this stoichiometry it is not probable that the catalytic oxidation of cyanide occurs simply through the decomposition of the copper(II) cyanide complex. The second-order dependence on hexacyanoferrate(III) can be explained by postulating a second step in which both $Fe(CN)_6^{3-}$ and $Cu(CN)_4^{2-}$ interact to form a binuclear CN^--bridged Fe(III)–Cu(II) cyanide complex:

$$Fe(CN)_6^{3-} + Cu(CN)_4^{2-} \xrightarrow{k_2} [(CN)_6FeCNCu(CN)_3]^{5-} \quad (16)$$

The bridging cyanide ion must be oxidized to

cyanate by a rapid transfer of two electrons, one each to the Fe(III) and Cu(II) central atoms respectively:

$$[(CN)_6FeCNCu(CN)_3]^{5-} + 2OH^- \xrightarrow{\text{fast}} Fe(CN)_6^{4-} + Cu(CN)_3^{2-} + CNO^- + H_2O \quad (17)$$

Such an oxidation of cyanide could consist of either a single two-electron step or two consecutive one-electron steps involving the formation of a transient cyanogen radical. To complete the catalytic cycle the copper(I) cyanide complex reaches its initial state:

$$Cu(CN)_3^{2-} + CN^- \xrightarrow{\text{fast}} Cu(CN)_4^{3-} \quad (18)$$

If reaction (16) is faster than the reverse of reaction (15) the steady-state treatment can be applied to the $Cu(CN)_4^{2-}$ species and, from this, the following rate equation can be obtained:

$$v^c = -\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{2k_a^c k_b^c [Cu(CN)_4^{3-}][Fe(CN)_6^{3-}]^2}{k_{-a}^c [Fe(CN)_6^{4-}] + k_b^c [Fe(CN)_6^{3-}]} \quad (19)$$

From the fact that k_{exp}^c is a linear function of $1/([Fe(CN)_6^{4-}] + [Fe(CN)_6^{3-}])$ it can be deduced that $k_{-a}^c \simeq k_b^c$ and the rate equation takes the simpler form:

$$v^c = \frac{2k_a^c [Cu(CN)_4^{3-}][Fe(CN)_6^{3-}]^2}{[Fe(CN)_6^{4-}] + [Fe(CN)_6^{3-}]} \quad (20)$$

In the initial stages we can affirm:

$$[Fe(CN)_6^{4-}] \ll [Fe(CN)_6^{3-}]$$

and equation (20) becomes:

$$v^c = 2k_a^c [Cu(CN)_4^{3-}][Fe(CN)_6^{3-}] \quad (21)$$

On the other hand, when the reaction is far enough advanced [or in the presence of a large excess of hexacyanoferrate(II)]:

$$[Fe(CN)_6^{4-}] \gg [Fe(CN)_6^{3-}]$$

and finally the rate equation will be:

$$v^c = \frac{2k_a^c [Cu(CN)_4^{3-}]}{[Fe(CN)_6^{4-}]} [Fe(CN)_6^{3-}]^2 \quad (22)$$

From the slope (k^c) of the plot of k_{exp}^c *vs.* copper concentration, a value for $k_a^c = 7.5 \times 10^3$ $l.mole^{-1}.min^{-1}$ was obtained. Values of the calculated and experimental pseudo second-order constants are in good agreement and are presented in Table 5.

Table 5. Values of the calculated and experimental pseudo second-order rate constants ($l.mole^{-1}.min^{-1} \times 10^{-2}$) for different copper concentrations

[Cu], $M \times 10^6$	k_{calc}^c	k_{exp}^c
2.0	6	7
4.0	12	14
6.0	18	18
8.0	24	23

($K_3Fe(CN)_6$, $5.0 \times 10^{-4}M$; NaCN, $1.0M$; NaOH $0.1M$; I, 2.0; T, 25°C)

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SHORT COMMUNICATIONS

VANADIUM(III) AS AN ANALYTICAL REAGENT: THE TITRIMETRIC DETERMINATION OF IRON, COPPER, THALLIUM, MOLYBDENUM, URANIUM, VANADIUM, CHROMIUM AND MANGANESE

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Summary—Vanadium(III) solutions can be used in direct titrations of iron(III), copper(II), thallium(III), molybdenum(VI), uranium(VI), vanadium(V), chromium(VI) and manganese(VII) in milligram amounts. The titrations are done at 70–80° for iron(III), copper(II), thallium(III), molybdenum(VI) and at room temperature for vanadium(V), chromium(VI) and manganese(VII). Uranium(VI) is titrated at 70–80° in presence of iron(II). The vanadium(III) solution is prepared by reduction of vanadium(V) to vanadium(IV) with sulphur dioxide, followed by addition of phosphoric acid and reduction with iodide, and is reasonably stable.

Vanadium(III) is a powerful reducing agent with a formal potential of $+0.359 \pm 0.002$ V *vs.* S.C.E. in dilute sulphuric acid.[1] However, vanadium(III) has seldom been used as a titrant mainly because the reactions are not sufficiently fast and the solutions are generally unstable. However, a reasonably stable vanadium(III) solution in sulphuric–phosphoric acid medium is easily prepared and quantitatively reduces a number of oxidizing agents rapidly. The present paper reports the preparation of the reagent and the titrimetric determination of iron(III), copper(II), thallium(III), molybdenum(VI), uranium(VI), vanadium(V), chromium(VI) and manganese(VII).

EXPERIMENTAL

Reagents

Vanadium(III) solution. Ammonium metavanadate (11.7 g) was dissolved in 1 litre of 1*M* sulphuric acid and reduced to vanadium(IV) with sulphurous acid. The excess of SO_2 was boiled off. Then 44.5 ml of syrupy phosphoric acid (s.g. 1.71) were added, followed by 13 g of hydriodic acid or 17 g of potassium iodide. The solution was boiled to remove iodine and to reduce the volume to less than 1 litre, then cooled and diluted to 1 litre. The solution was standardized against standard potassium dichromate solution, with barium diphenylaminesulphonate as indicator. Aqueous solutions of copper sulphate, thallium sulphate, uranyl acetate, sodium molybdate, ammonium vanadate and potassium dichromate were prepared and standardized by the usual methods.[2]

Procedures

Iron. A portion of iron(III) solution containing 0.631–1.262 mg of Fe was diluted to 50 ml with distilled water, heated to 70–80° and titrated with vanadium(III) solution to a colourless or faint-green end-point in the presence of thiosalicylic acid as indicator.

Copper. A portion of standard copper sulphate solution containing 0.622–1.244 mg of Cu was transferred to a conical flask, 8 ml of 10*M* hydrochloric acid and 3 g of potassium chloride were added, the solution was diluted to 20 ml, heated to 70–80° and titrated with vanadium(III) solution to a violet end-point in the presence of two drops of mixed indicator (0.02% phenosafranine and 0.05% Methylene Blue in water).

Molybdenum. A portion of an aqueous solution of sodium molybdate containing 0.978–1.966 mg of Mo was added to 20 ml of 6*M* hydrochloric acid in a conical flask, along with two drops of 0.02% aqueous phenosafranine solution as indicator. It was heated to 70–80° and titrated with vanadium(III) solution to the violet end-point.

Thallium. A portion of standard thallium(I) solution was placed in the titration vessel and saturated bromine water was added dropwise until the solution became faintly yellow. After 5 min, 3 or 4 drops of a 10% solution of pure phenol in glacial acetic acid were added to the solution. The solution was then diluted to 20 ml with 2*N* sulphuric acid, heated to 70–80° and titrated slowly with vanadium(III) solution to a colourless or faint-green end-point in the presence of two drops of phenosafranine indicator. The procedure was identical for thallium(III) except for the addition of bromine water and phenol.

Uranium. A portion of a solution of uranyl acetate in 2*M* acetic acid was added to 20 ml of 2*N* sulphuric acid, heated to 70–80° and titrated slowly with vanadium(III) solution to a faint-green end-point in the presence of a drop of iron(III) solution and two drops of phenosafranine indicator.

Vanadium. A portion of a solution of ammonium vanadate in 2*N* sulphuric acid was added to 20 ml of 2*N* sulphuric acid and the mixture was titrated with vanadium(III) solution in the presence of 3–4 drops of barium diphenylaminesulphonate as indicator to a bluish-green end-point.

Manganese. A portion of a standard solution of potassium permanganate was placed in the titration vessel, diluted to 25 ml with distilled water and titrated with vanadium(III) solution. After the solution had become decolourized one drop of 0.2% phenylanthranilic acid was added and the titration continued until the colour changed from violet to green.

Table 1. Determination of iron(III), copper(II), thallium(III), molybdenum(VI), uranium(VI), vanadium(V), chromium(VI) and manganese(VII)

Metal ion	Taken, *mg*	Found,* *mg*	Std. devn., *mg*
Fe(III)	0.631	0.643	0.009
	1.262	1.256	0.004
Cu(II)	0.622	0.617	0.006
	1.244	1.251	0.002
Tl(I)	0.993	1.007	0.010
	1.986	1.975	0.005
Tl(III)	0.935	0.944	0.006
	1.870	1.861	0.010
Mo(VI)	0.978	0.982	0.002
	1.956	1.967	0.010
U(VI)	1.187	1.180	0.006
	2.374	2.391	0.011
V(V)	1.016	1.018	0.005
	2.032	2.030	0.003
Cr(VI)	0.490	0.493	0.001
	0.980	0.978	0.002
Mn(VII)	0.646	0.647	0.002
	1.292	1.288	0.005

* Mean of 3–5 determinations

Iron and manganese in manganese ore. A 2-g sample (British Chemical Standard) was dissolved in 6*M* hydrochloric acid and the solution was evaporated to dryness. The residue was kept in an air-oven at 110–115° for an hour, cooled to room temperature, dissolved in water acidified with hydrochloric acid, warmed, filtered into a 250-ml standard flask and diluted to volume.

A known volume of this solution was heated to 70–80° and the iron was titrated with vanadium(III) solution, with thiosalicylic acid as indicator. To a further portion (10 ml), 10 ml of 12*N* sulphuric acid, 1 ml of phosphoric acid (s.g. 1.71) and 0.5 g of ammonium persulphate were added and it was heated to boiling to decompose excess of persulphate, cooled and titrated with vanadium(III) solution as for manganese.

The first titration gave the iron content and the second the sum of iron and manganese.

RESULTS AND DISCUSSION

Gooch and Curtis[3] obtained vanadium(III) by reducing vanadium(V) with hydriodic acid, but in the present work it was found that the yield was low and the iodine difficult to remove. It was also found that the yield was quantitative if vanadium(V) was first reduced to vanadium(IV) with sulphur dioxide and the vanadium(IV) was then further reduced with iodide in ~0.7*M* phosphoric acid medium. Attempts at direct reduction of vanadium(V) with iodide in phosphoric acid medium led to a solid yellowish green phosphate complex of a lower oxidation state of vanadium; this is being investigated and will be reported on elsewhere. The vanadium(III) solution prepared as described is stable for 3–4 days but then begins to deteriorate by 0.1–0.2% Its stability is improved by storage at 10–15°.

The results for the analyses are shown in Table 1. The reaction of vanadium(III) with iron(III), copper(II), molybdenum(VI) and thallium(III) to give vanadium(IV) is fast at 70–80°, so these metals can be determined quite easily. Reduction of uranium(VI) is rather slow but the titration is feasible in presence of a little iron(II). Oxidants such as vanadium(V), chromium(VI) and manganese(VII) rapidly oxidize vanadium(III) at room temperature.

Table 1 shows that milligram quantities of the metals can be determined quantitatively by direct titration with vanadium(III) and the precision is sufficiently good for routine analysis.

Application of the method to the determination of iron and manganese in manganese ore gave values for iron and manganese of 5.3% (Certificate value 5.2%) and 49.2% (Certificate value 49.0%) respectively.

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DETERMINATION OF CHROMIUM IN CHROME ORES

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Summary—A method for the estimation of chromium in chrome ores is reported. Manganese dioxide or manganese ore in the presence of 9*M* sulphuric acid is used for the oxidative decomposition of different grades of chrome ores. The results compare favourably with those obtained by standard methods.

The analysis of chrome ores and chrome-bearing refractories has been the subject of considerable study. The methods based on peroxide fusion are tedious and proper care has to be taken to get reproducible results. Chromium in chrome minerals is generally estimated by bringing it into solution by either an alkaline or acidic treatment and then analysing by a standard method. Basic attack involves fusion of the ore with sodium peroxide[1a] or a suitable alkali mixture and titrimetric determination of the resultant Cr(VI) with ferrous ammonium sulphate solution. Acidic attack involves decomposition of the ore with a mixture of sulphuric acid and perchloric acid[2] or phosphoric acid.[3] The chromium(III) produced in the latter case is estimated after oxidation to Cr(VI). Decomposition in the presence of perchloric acid is frequently chosen for determination of Fe, Ca, Al, and Mg rather than for chromium.[4a] Earlier work from these laboratories reported the use of Mn(IV) as an oxidimetric reagent.[5] A recent patent[6] suggested the possibility of employing manganese ore for converting the chromium(III) oxide of chrome ore into chromium(VI). However, the quantitativeness of this reaction has not been investigated. Preliminary experiments have shown that MnO_2 or manganese ore can quantitatively oxidize chromium(III) in the presence of sulphuric acid, suggesting a simple method for the estimation of chromium in chrome ores. The present communication describes the experimental conditions for carrying out such an analysis.

EXPERIMENTAL

Reagents and materials

Standard chromite. Grecian BCS 308.

Chromite. Low, medium and high grade from Sukinda region of Orissa, India.

Manganese ore. Different grades from Tirode mines (Madhya Pradesh) of Manganese Ore (India) Ltd.

Manganese dioxide. Commercial and pure.

General procedure

Weigh accurately 100 mg of the finely powdered sample of chrome ore, previously dried at about 110°. Add 300 mg of manganese ore or 200 mg of manganese dioxide and mix thoroughly with a glass rod. Add 25 ml of sulphuric acid (1 + 1) and stir well. Cover the beaker and heat it on a hot-plate till the appearance of white fumes. Cool and dilute with 50 ml of water and heat the mixture for a further 30 min to ensure complete oxidation of Cr(III). Adjust the pH of the solution to about 1 with ammonia or sodium hydroxide and boil the solution for some time. Alternatively, dilute to 400 ml with water and boil for some time. Cool, allow to settle and filter through a Whatman No. 30 filter paper. Determine the chromium content by titrating with 1*M* ferrous ammonium sulphate in presence of barium diphenylamine sulphonate as an indicator (1 ml of titrant is equivalent to 25.34 mg of Cr_2O_3).

RESULTS AND DISCUSSION

Typical results for the determination of chromium in chrome ores using manganese dioxide and manganese ore of different grades are shown in Table 1. The results for the determination of chromium(III) in chromium(III) sulphate solution are given in Table 2.

In acid medium chromite can be decomposed by heating with powerful reagents such as perchloric acid, mixtures of sulphuric acid and perchloric acid[7] or phosphoric acid, or with sulphuric acid alone (under pressure).[8] Heating with concentrated hydrochloric or sulphuric acid and hydrofluoric acid has also been used.[4b] Methods involving perchloric acid are preferred for estimation of constituents other than chromium.[1b] The same is true for use of sulphuric acid under pressure. Chromium(III) is formed when a sulphuric/phosphoric acid mixture is used. In the proposed method manganese dioxide acts as the oxidizing agent and facilitates the quantitative decomposition of chrome spinel. The manganese dioxide reacts with sulphuric acid to give manganese(IV), which is a strong oxidizing agent. The standard potentials of the systems $Mn(IV) + 2e \rightleftharpoons Mn(II)$, $Mn(IV) + e \rightleftharpoons Mn(III)$ and $Mn(III) + e \rightleftharpoons Mn(II)$ are 1.577, 1.62 and 1.511 V respectively,[9] whereas the formal potential of the Cr(VI)/Cr(III) system is 8*M* sulphuric acid is 1.35 V.[10] It is probable that manganese(IV) sulphate oxidizes the chromium(III) to chromium(VI). In the presence of phosphoric acid Mn(IV) is unstable and the manganese(III) phosphate complex cannot oxidize chromium(III). Manganese(IV) sulphate is not stable at lower acidity and easily hydrolyses. Manganese hydroxide adsorbs chromium(VI), especially at higher pH. Therefore after the oxidation reaction, the manganese is precipitated by boiling after adjustment of the pH to 1 or sufficient dilution of the solution. Manganese dioxide is the oxidizing agent and can be employed either as the chemical or in the form of naturally occurring manganese ore. Such manganese ores are readily available in India and some other countries. The results in Table 1 show that any type of chrome ore (low, medium or high grade) can be analysed for its chromium content by the present method. The observed values are comparable to those obtained by standard procedures. The method can also be used for determination of Cr_2O_3 and chromium(III) in solutions. The method is simple and rapid and can be

Table 1. Determination of chromium in chrome ore and pure Cr_2O_3

Sample	Certified Cr_2O_3 content %	Cr_2O_3 content found, % I	II	III	IV
High-grade chrome ore	53.45	53.3	53.3	53.4	53.3
Medium-grade chrome ore	35.12	35.0	35.0	35.1	35.0
Low-grade chrome ore	28.62	28.5	28.5	28.5	28.4
Grecian chrome ore (BCS grade)	41.50	41.4	41.4	41.5	41.4
Pure Cr_2O_3	99.72	99.7	99.6	99.7	99.5

Oxidant: I, high-grade Mn ore, MnO_2 81.2%, P 0.26%; II, low-grade Mn ore, MnO_2 47.5%, P 0.7%; III, BCS Standard 176/1, MnO_2 73.4%, P 0.14%; IV, pure MnO_2.

Table 2. Determination of chromium(III) in solution as sulphate

Oxidizing agent	Amount taken, *mg*	Amount found, *mg*
High-grade Mn ore	25.2	25.4
Low-grade Mn ore	20.2	20.0
BCS ore	10.1	10.2
Pure MnO_2	25.2	25.1

completed in about 2 hr. The principal advantage is that chromium(VI) is produced in acid medium and can be directly titrated. No hazards are involved and no special precautions are necessary. Further work on the kinetics of the reaction and its application to direct preparation of chromic acid by the use of manganese dioxide or manganese ore is now in progress.

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THE RING–AIR TECHNIQUE: AN ALTERNATIVE TO THE RING-OVEN TECHNIQUE IN CIRCULAR THIN-LAYER CHROMATOGRAPHY

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Summary—A technique is described in which a ring of air is used to produce sample concentration by solvent evaporation on high-performance thin-layer chromatography plates. The technique is compared to the ring-oven technique and both are evaluated by using a dye mixture. Both techniques are employed to reduce the size of relatively large spots on the plates in an attempt to match the resolution obtained from small spots in circular chromatography.

The ring-oven technique is a useful method of concentrating substances in thin-layer and paper chromatography and so lowering very effectively the detection limit.[1] The technique has been used largely for inorganic substances, but finds application in organic chemistry as well.

In one form of the method filter paper or a thin-layer plate is placed on a ring-shaped oven and the sample is spotted in the centre. The soluble portion of the sample is washed out (with a suitable solvent added through a capillary tube) to the hot ring-oven front where the solvent evaporates and concentrates the dissolved sample. In general the oven temperature should be a few degrees above the boiling point of the solvent used for washing.[1]

In another form of the method[2] a ring-oven is placed on the back of a thin-layer plate and a spot of sample, centrally placed on the adsorbent side, is washed to the heated front which is transmitted through the glass from the ring-oven. The idea behind this "thermal focusing" is to narrow the initial band (*i.e.*, sample) width and so improve resolution in the subsequently developed chromatogram. The ring-oven is placed on the glass side of the thin-layer plate for convenience and probably in an attempt to avoid any disturbance of the adsorbent since this might effect resolution, especially in high-performance thin-layer chromatography. A case has been reported where the ring-oven is placed directly on the adsorbent.[1,3] Very little quantitative information, however, is available on these approaches.

One of the drawbacks of the technique is that it cannot be applied to volatile substances in aqueous or high boiling point solvents, or to thermolabile substances such as enzymes, since the temperature required to evaporate the solvent and so deposit the substance can result in volatilization or decomposition of the latter.

Alternatives to the ring-oven technique for temperature-sensitive substances have been tried[4]—one of them employing a so-called adsorption barrier.[5] In this method the ring-oven is used only to prepare a filter paper with a narrow ring of a suitable adsorbent. The heat-sensitive substance (*e.g.*, an enzyme) is transferred in a solvent to the adsorption zone by use of a washing ring. This approach, however, is not possible with thin-layer plates and does not allow subsequent conventional development by circular chromatography, which is one extension of the ring-oven technique.

A less complicated alternative for temperature-sensitive substances is to use a ring of air to produce evaporation and concentration.

This contribution describes the construction of a small-scale ring–air apparatus and compares its performance, for a dye mixture, with that of the ring-oven technique. The possibility is examined of using both techniques to concentrate relatively large sample spots on high-performance thin-layer plates in order to match the resolution, obtained in subsequent circular chromatography, with that obtained from small spots.

EXPERIMENTAL

Ring–air apparatus

Figure 1 illustrates the apparatus used. An air-pump forces air into a chamber from which it flows through an annular outlet. Down the centre of the outlet is a syringe needle carrying the washing solvent. The syringe needle, with a square-cut tip, is held in place with a small Teflon sleeve and attached to a syringe (e.g.., 25 μl volume) by

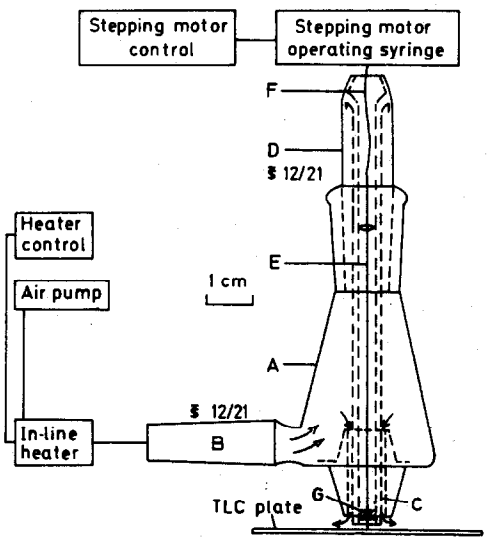

Fig. 1. Ring–air apparatus, constructed of glass. A = air chamber; B = air inlet; C = annular air outlet; D = removable central tube carrying syringe needle; E = syringe needle; F = Teflon connecting tube; G = Teflon sleeve holding needle. Arrows indicate air-flow direction.

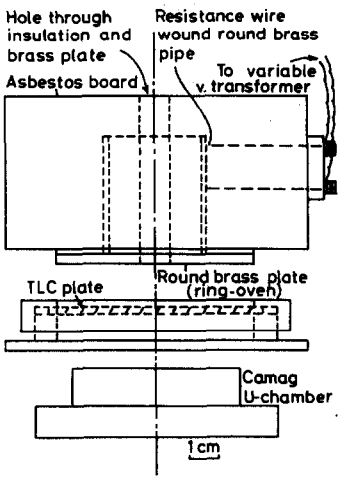

Fig. 2. Ring-oven apparatus.

means of a Teflon tube. A stepping motor activates the syringe plunger and if the rate of the stepping motor is varied by the control unit (and also by using different sizes of syringe), any desired flow-rate of solvent can be obtained. The stepping motor and control unit are derived from the Camag U-chamber system (Camag, Switzerland).

The ring–air apparatus can be used with high boiling point solvents. If necessary the air can be heated by an in-line heating element.

The operation of the apparatus is as follows. The sample is spotted on a thin-layer plate at discrete points on a circle of diameter as small as practicable without producing arc over-lapping during the washing process used. The sample spot is dried and the plate placed with the syringe needle immediately above the centre of the circle. The needle tip should protrude about 0.5 mm beyond the supporting glass jacket. The Teflon sleeve is positioned at least 2 mm from the needle tip to counteract creep-back up the needle. By means of bolts running through springs supporting the heating element, the air-chamber and needle can be lowered perpendicularly so that the needle is slightly above the thin-layer plate.

Ring-oven apparatus

The oven built is shown in Fig. 2. In use the oven is placed on the back of a thin-layer plate held in the Camag U-chamber system.

Procedure

Experiments were performed with a 0.49% w/v solution (in toluene) of a mixture of indophenol blue, Sudan Red and Butter Yellow spotted on silica gel HPTLC plates. Two makes of plates were used—Merck 60 and Macherey-Nagel SIL-20.

Experimental conditions were as follows:

(*i*) volume (spotted) varied, concentration constant;
(*ii*) volume varied, weight of dye loaded constant;
(*iii*) volume constant, concentration varied.

The dye mixture was concentrated as follows. The plate was placed under the ring-air and ring-oven apparatus and the sample washed with a solvent that would carry all the components with it, in this case n-butanol (b.p. 118°). The sample was washed to the ring of air or edge of the oven where it evaporated and left the sample concentrated in the form of a thin arc. A plate temperature of 80° was used for the ring-oven (thermometer placed through the hole in the oven). In the ring–air experiments it was not found necessary to use heated air.

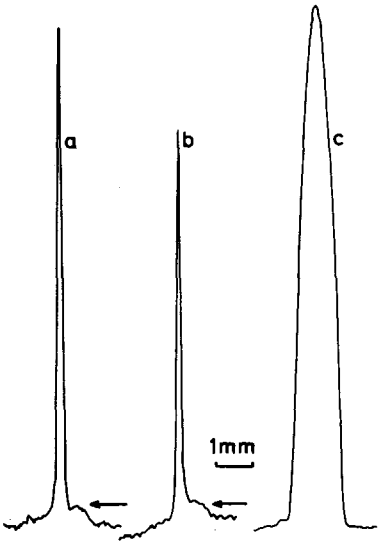

Fig. 3. Densitometer curves showing width of concentrated sample arcs produced by the ring–air (*a*) and ring-oven (*b*) techniques compared to the width of a conventionally spotted sample (*c*), in all cases for a 1-μl application on Macherey-Nagel SIL-20 plates. The arc widths were measured in the direction of solvent flow, which is indicated by the arrows. Dye concentration was 0.12% w/v.

The washing process was stopped when the sample appeared optimally concentrated, and the plate left in the apparatus to allow complete removal of solvent. After equilibration with the atmosphere, the plate was transferred to the U-chamber and developed in the normal way with toluene. A modification to the U-chamber control unit was the addition of a switch to enable the stepping-motor rate to be halved. Using the slowest speed during development resulted in improved resolution.

RESULTS AND DISCUSSION

The chromatograms were evaluated with a Vitatron TLD 100 Densitometer in the transmission mode. Resolution between adjacent peaks was determined in the usual way, *viz.* twice the peak separation distance divided by the sum of the peak widths at their base.

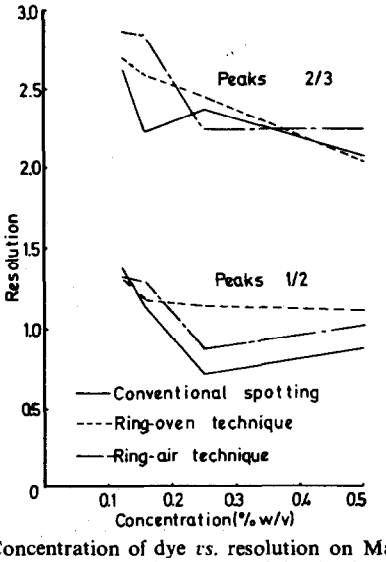

Fig. 4. Concentration of dye *vs.* resolution on Macherey-Nagel HPTLC plates; 1 μl of dye loaded.

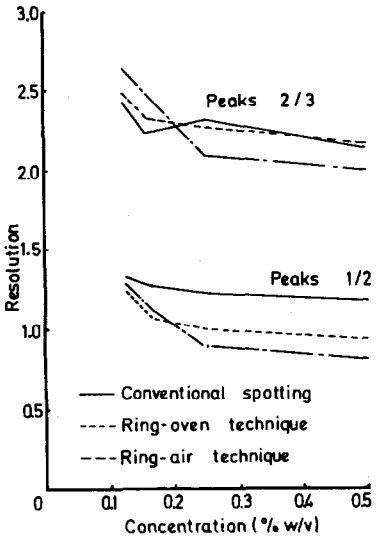

Fig. 5. Concentration of dye *vs.* resolution on Merck HPTLC plates; 1 μl of dye loaded.

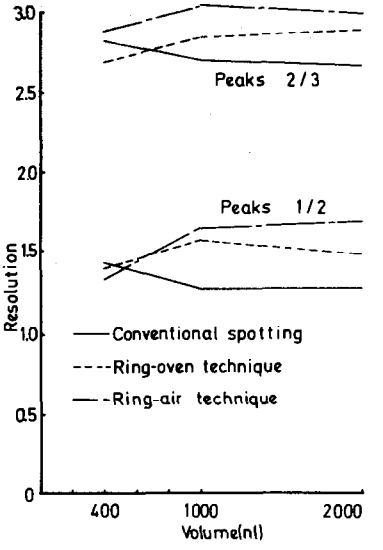

Fig. 7. Volume of dye spotted *vs.* resolution on Merck HPTLC plates. Weight of dye loaded was constant. Determinations were done in duplicate with a mean relative error for the different methods as follows: conventional spotting 6%; ring-oven technique 5%; ring-air technique 4%.

Shown in Fig. 3 are densitometer curves of the concentrated sample arcs (*i.e.*, before chromatographic development) and of a conventionally spotted sample, in all cases for a 1-μl sample. The important feature is the narrowness of the arcs compared to the sample spot.

Figures 4–7 illustrate the chromatographic results as graphs of resolution *vs.* sample volume or concentration used.

A comparison of the results in Figs. 4 and 5, which were obtained on different plates, shows that resolution improves with lower concentration. Although the curves have been drawn for single determinations, the fact that they vary in much the same way is felt to indicate that they are a reliable guide.

The reason why conventional spotting produces a poorer resolution compared to the other techniques for the peak pair 1/2 on the Merck plate, whereas the reverse occurs on the Macherey-Nagel plate, is probably due to overloading of the Merck plate, samples showing a pronounced tailing on it. This plate has a harder adsorbent coating and is slightly thinner (5%) than the Macherey-Nagel plate. It is not possible from an examination of Figs. 4 and 5 to say which technique offers the better resolution.

When the concentration is constant but the volume variable (Fig. 6), the resolution improves with smaller volume spotted on the plate. Again no decision can be made as to which technique provides the best resolution.

Finally, when the weight of sample loaded is kept constant but the volume (and hence concentration) is varied (Fig. 7) the resolution remains approximately constant. The ring-air technique would seem to provide the best overall resolution.

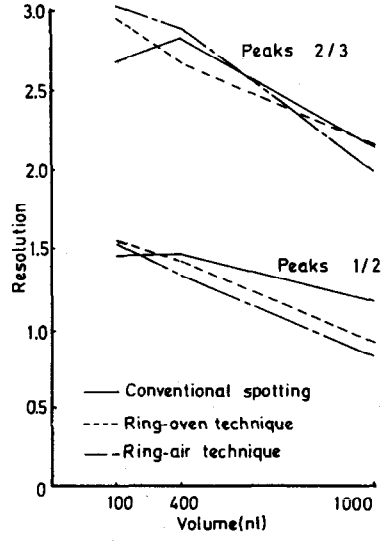

Fig. 6. Volume of dye spotted *vs.* resolution on Merck HPTLC plates. Concentration constant at 0.49% w/v.

CONCLUSIONS

The following facts emerge from this study:

(*i*) The ring–air technique is as good as the ring-oven technique for concentrating substances. For dealing with heat-labile substances the ring–air technique is the obvious choice because of the use of cool air. Examples of heat-labile substances are enzymes and the carbamate pesticides.

(*ii*) The use of the ring–air and ring-oven techniques to concentrate large spots into a narrow arc does not appear to have any advantage over conventional spotting where resolution in the subsequent chromatogram is concerned.

(*iii*) Conclusion (*ii*) probably holds only for high-performance thin-layer plates. It appears likely that the two concentration techniques will have an advantage over conventional spotting when plates with a thick adsorbent coating are used, as overloading will be less likely to occur.

The ring–air apparatus described can probably be adapted in the ways mentioned by Weisz[1] for the ring-oven technique, *e.g.*, for improving resolution by superimposing the apparatus on selected areas of a normally developed linear TLC chromatogram. A modification of the apparatus to produce a curtain of air along a straight front would enable large samples to be concentrated in linear

TLC prior to development. This approach, with a different experimental arrangement, has been shown to improve subsequent chromatographic resolution.[6]

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SPECTROPHOTOMETRIC DETERMINATION OF MICRO AMOUNTS OF URANIUM

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Summary—Uranium(VI) in the presence of numerous cations and anions is determined by the iron(II)–phosphoric acid–Ferrozine method at concentrations of 8–75 μg/25 ml with a relative precision of 3–1%.

Determination of uranium in the presence of various metals has been of wide interest, and numerous methods have been published.[1] Several spectrophotometric methods for the determination of small amounts of uranium have been reported: Bustamante and Delgado,[2] Yamamoto,[3] Puzanowska-Tarasiewicz *et al.*,[4] and Dubey and Nadkarni[5] have used extraction procedures and formation of coloured chelates. Vydra and Přibil[6] and Riggs[7] have used iron(III) in the presence of 1,10-phenanthroline to oxidize uranium(IV). Gayer and Lifshitz[8] oxidized uranium(IV) with iron(III) and determined the resultant iron(II) with ferricyanide. The 1,10-phenanthroline–iron(III) method appears to be relatively simple and sensitive. The method described in this note allows the determination of small amounts of uranium in the presence of large amounts of iron by using iron(II) to reduce the uranium(VI) in concentrated phosphoric acid, as reported by Rao and Sagi,[9] Walker and Vita,[10] and Mareska.[11] This reduction is followed by the selective oxidation of iron(II) with nitric acid and finally the oxidation of uranium(IV) by iron(III) in the presence of Ferrozine, which reacts with the iron(II) produced. The absorbance of this complex is then a measure of the amount of uranium.

The solubility of Ferrozine in water, and the high molar absorptivity of the iron(II)–Ferrozine complex, 2.8×10^4 l.mole^{-1}.cm^{-1}, renders this reagent useful for the determination of micro amounts of uranium.

EXPERIMENTAL

Reagents

Reagent grade uranyl acetate was used to prepare a stock solution by dissolution of 1.060 g of it in 20 ml of 6*M* sulphuric acid and dilution to 250 ml. This solution was standardized by the dichromate method.[12] A 0.02*M* Ferrozine solution was prepared by dissolving 0.52 g in 50 ml of demineralized water. Fresh solutions were prepared every week.

A buffer solution of pH 3.5 was prepared by dissolving 28.5 g of reagent grade monochloroacetic acid in 900 ml of demineralized water, and adjusting the pH with concentrated sodium hydroxide solution.

The other reagents were prepared from reagent grade chemicals. The ferrous ammonium sulphate solution was prepared in 1*M* sulphuric acid, and the ammonium molybdate solution in 0.1*M* sodium hydroxide.

Procedure

A portion (0.25–0.50 ml) of uranium sample was transferred to a 25-ml standard flask containing 0.25 ml of 1.5*M* sulphamic acid, 0.25 ml of 0.5*M* ferrous ammonium sulphate, and 2–3 ml of concentrated phosphoric acid. (The phosphoric acid concentration in the mixture must be at least 12*M*.) The mixture was heated for 2 min in a hot water-bath (60–70°) and mixed. The mixture was removed from the bath and allowed to cool for 1 min to approximately 40–45°. To this solution the following reagents were added: 0.25 ml of 4*M* nitric acid–0.1*M* sulphamic acid mixture, two drops of 1% ammonium molybdate solution, and 1.5 ml of 85% phosphoric acid. The solution was then held at 40° for 5 min and stirred vigorously for 30 sec to allow the gas bubbles to escape. Immediately after this, 5 ml of 0.02*M* Ferrozine were added, followed by the addition of 10 ml or less of 6 or 8*M* ammonia solution (depending on the amount of phosphoric acid used), until a slight cloudiness formed, and the pH was raised to approximately 3.2–3.3. At pH values higher than 3.2, iron(III) formed a precipitate which was eliminated by the addition of a few drops of phosphoric acid. Then 5 ml of 1*M* buffer solution were added; the solution was diluted to the mark and the absorbance was measured at 562 nm against a blank.

RESULTS AND DISCUSSION

The reactions for the determination of uranium using phosphoric acid method are summarized below:

$$UO_2^{2+} + 2Fe^{2+} + 4H^+ \xrightarrow[H_3PO_4]{11\text{–}13M} U^{4+} + 2Fe^{3+} + 2H_2O \quad (1)$$

$$U^{4+} + 2Fe^{3+} + 2H_2O \xrightarrow[1\text{–}3]{pH} UO_2^{2+} + 2Fe^{2+} + 4H^+ \quad (2)$$

$$Fe^{2+} + 3\text{Ferrozine} \xrightarrow{pH>3} [Fe(\text{Ferrozine})_3]^{4-} \quad (3)$$

Uranium(VI) becomes a stronger oxidant than iron(III) as the concentration of phosphoric acid increases. Thus, complete reduction of UO_2^{2+} with iron(II) is achieved in 11*M* or more concentrated phosphoric acid solutions. The reaction is complete in about 2 min at 70°. After this reaction is completed the excess of iron(II) is preferentially oxidized by nitric acid at 40° in the presence of molybdate as a catalyst, and of sulphamic acid. This oxidation is to be carried out at temperatures below 45°, otherwise some of the uranium(IV) will also be oxidized. After cooling of the solution and elimination of nitrogen oxides the pH is raised to approximately 3.0. In the pH range 1–3 uranium(IV) is readily oxidized to uranium(VI) by iron(III) in the presence of Ferrozine. The final pH is adjusted to above 3.1–3.2, the range where not only is the formation

Table 1. Effect of foreign ions on the amount of uranium found

Foreign ion Type	Amount, μg/ml	Uranium found,* μg/ml
Bi(III)	83.6	2.38 ± 0.03
Co(II)	1.0	2.52 ± 0.01
Cu(II)	25.4	2.40 ± 0.03
Hg(II)	80.4	2.37 ± 0.03
Ni(II)	58.8	2.38 ± 0.07
Zn(II)	26.0	2.38 ± 0.01
Pb(II)	41.4	2.39 ± 0.05
W(VI)	73.6	2.40 ± 0.05
Th(IV)	92.8	2.39 ± 0.02
SO_4^{2-}	100.0	2.40 ± 0.02
Cl^-	36.0	2.39 ± 0.04
NO_3^-	62.0	2.38 ± 0.02

* Mean and range of 5 determinations. All samples contained 2.38 μg/ml.

of iron(II)–Ferrozine complex complete, but also iron(III) is kept in solution.

The apparent molar absorptivity of the iron(II)–Ferrozine produced by the reaction of uranium(IV) with iron(III) corresponds to $5.59 \pm 0.04 \times 10^4$ l.mole^{-1}.cm^{-1} with respect to uranium; the theoretical value is 5.6×10^4. These values are readily reproduced with a relative precision ranging from 4% at 0.3 ppm to better than 1% at 1-ppm levels.

The effect of various ions on the uranium determination is shown in Table 1.

In this method, iron and many other metal ions such as bismuth, mercury, lead, zinc, tungsten, thorium and copper do not interfere. In the presence of large amounts of zinc, nickel, chromium(III), and cadmium an additional amount of Ferrozine is to be added. Uranium in the presence of large amounts of copper yields somewhat higher results. Cobalt interferes seriously and must be eliminated. Alkali metals and rare earth metals do not interfere. Common anions such as phosphate, sulphate, chloride and nitrate do not interfere. In the phosphate method, more of the metal ions can be tolerated than in the lead reductor method.

However, the lead reductor method shows somewhat better precision, since it does not require as many chemical operations as the phosphoric acid method. The phosphoric acid method is relatively fast and sensitive. It requires approximately 10 min for each sample and is almost 2.5 times more sensitive than the iron(II)–1,10-phenanthroline method.

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DETERMINATION OF TELLURIUM IN GEOCHEMICAL MATERIALS BY FLAMELESS ATOMIC-ABSORPTION SPECTROSCOPY

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Summary—A method is described for the determination of tellurium at nanogram levels in rocks and in other complex materials by the use of flameless atomic-absorption spectroscopy. A very selective organic extraction procedure is applied to avoid matrix interference effects during extraction of Te and the atomization stage in the graphite furnace. Prior separation of iron and other interfering elements is achieved by a combined cupferron–ethyl acetate extraction. Tellerium is extracted from 6*M* hydrochloric acid with MIBK and stripped into aqueous medium. Pipetting of the aqueous extract into the graphite furnace gives fairly good instrumental reproducibility (2–3% error). Detection limits of about 10 ppM Te for a 0.5-g sample have been achieved with the medium-performance apparatus used. Results for Te in some geochemical reference materials are reported. Indications are given for the determination of Sb and Mo in the same solutions.

Until very recently data on the distribution of tellurium in non-mineralized silicate rocks have been practically non-existent. The 1973 tables of elemental abundances in geological materials[1] reported for tellurium only the upper abundance limit (< 1 ppm) for a limited number of samples. The lack of data on Te abundances accounted essentially for the difficulties in developing a method to determine this element at nanogram levels in materials with a very complex matrix such as silicate rocks. In recent years more sophisticated techniques such as neutron activation,[2] isotope-dilution mass spectrometry[3] and atomic-absorption spectroscopy (AAS) have been employed to analyse geological materials for Te. With this last technique Te has been detected at nanogram levels by using the sampling-boat system[4] and the graphite furnace.[5] The recently introduced hydride system may undoubtedly give a valuable improvement in analysis for Te in rocks because of its simplicity and sensitivity. Nevertheless, the graphite furnace has the unique advantage that the same test solutions can be used for determining other trace elements. This paper describes a stepwise chemical separation method for Te from silicate matrices and subsequent analysis for Te by use of a heated graphite atomizer. Included are some data regarding the determination of Sb and Mo in the same analytical solution.

General analytical comments

The major difficulty in the determination of Te and, in general, of trace elements in rock samples by use of the graphite furnace is the necessity for separation of these elements from the major elements constituting the silicate matrix. If this is not done, the analysis may be affected by errors that even apparently adequate procedures such as standard-addition methods cannot minimize. Tellurium is usually separated from other elements by organic solvent techniques. The extraction from fairly concentrated hydrochloric acid medium is easy,[6] but not very specific and many other elements follow Te into the organic phase. On the one hand this may affect the efficiency of the Te extraction and on the other lead to high background absorption during subsequent atomization in the graphite furnace. Of the elements extracted together with Te from 6*M* hydrochloric acid, iron is by far the most important since it is almost totally extracted and is usually a major constituent in geological materials. None of the other co-extracted elements[6] is normally present in rocks in sufficient amount to cause interference. A previously reported procedure for determination of Te in rocks, based on a simple extraction with MIBK (methyl isobutyl ketone) and use of a standard-addition method[5] was found not of general application because of matrix interference effects. Our initial attempts at directly pipetting the MIBK extract into the furnace were unsuccessful in most cases, because of high background absorption exceeding the background-correction capabilities of the instrument used. This difficulty may be overcome only by using a very selective extraction procedure for tellurium.

Separation of tellurium from interfering elements

As iron is the only element which may seriously affect the efficiency of Te extraction by MIBK, its interference effects were investigated by double extraction of 5-ppM Te solutions containing various amounts of iron. Tellurium recovery in the first and second MIBK extracts is shown in Fig. 1 (the absorption was measured after complete chemical treatment as reported below). Removal of Te into the MIBK phase in the first extraction decreases strongly with increasing Fe content but increases in the second extraction. This means, of course, that the presence of large amounts of iron (above ~400 ppm) inhibits extensive extraction of Te by MIBK and that this last becomes effective only if most of the iron is previously extracted. Many highly efficient iron extractants are known but in our case a supplementary condition is the non-removal of tellurium. After a series of experiments with various extractants a cupferron–ethyl acetate extraction was found to give the best selective removal of iron from hydrochloric acid media containing Te, as shown by B in Fig. 1. Recovery of Te was > 80% and independent of the original iron concentration.

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It is well known that the reproducibility of absorption signals obtained by use of the graphite furnace is a function of the medium used, and is often poorer for organic than for aqueous solutions. There may be several reasons for this, such as the increased difficulty in pipetting organic solutions, or spreading or irregular absorption of the organic solvent in the tube before drying. For this reason aqueous solutions are, when possible, preferred. Tellurium present as the chloride complex in the MIBK phase is easily stripped into an aqueous phase with $<0.8M$ hydrochloric acid concentration. As the stripping is also effective with high organic-aqueous volume ratios, very small final volumes of analytical solutions can be used, thus increasing the analytical sensitivity. A working curve obtained by pipetting constant volumes (20 μl) of 0.5–10 ppM Te solutions (after the complete extraction cycle) was found to be linear. We recommend the pipetting of constant volumes of solution to avoid any error inherent in possible dispersion of solution along the tube.

As tellurium may be partially lost before the atomization stage a matrix modification technique[7–10] was tried, nickel being added to the analytical solution after the complete extraction cycle, but without much improvement. This suggests that at the charring temperature used loss of Te by volatilization does not occur. Besides Fe and Te, many other metals are extracted by cupferron–ethyl acetate[11,12] and MIBK,[9] including the geochemically important trace elements Au, Tl, Ge, Sb, Mo, As, Pt which are thus potentially determinable in the solution used for the Te determination. Preliminary investigations on Mo and Sb were encouraging. Both are almost totally (>90%) extracted with cupferron–ethyl acetate and are easily stripped in the same way as Te. Precedures for determination of some of these elements will be reported elsewhere.

EXPERIMENTAL

Apparatus

A Perkin–Elmer Model 306 atomic-absorption spectrophotometer with a Model 56 recorder, a Perkin–Elmer Intensitron® tellurium lamp, and a Model HGA-2000 furnace equipped with a deuterium background corrector were used.

Operating conditions

Spectrophotometer

Wavelength	214.3 nm
Spectral band-width	0.2 nm
Scale expansion	1x

HGA module

Drying temperature	150°	15 sec
Charring temperature	600°	35 sec
Atomization temperature	2035°	12 sec
Argon flow	4 meter divisions, interrupted	
Sample volume	20 μl	

Reagents and standards

Tellurium certified atomic-absorption standard (1000 μg/ml) was obtained commercially. Working standards (0.2, 0.51, 1, 5, 10 ng/ml) were prepared by diluting the concentrated standard with demineralized water. Superpure concentrated reagent grade hydrofluoric, nitric and hydrochloric acids (Merck) were used.

Procedure

Weigh a 0.5-g powdered sample into a 50-ml Teflon vessel,[13] add 1 ml of *aqua regia* and swirl the vessel to wet the sample, then add 10 ml of concentrated hydrofluoric acid, evaporate to dryness on a hot-plate at 100–110°, add 0.5 ml of *aqua regia* and 5 ml of hydrofluoric acid to the residue and repeat the digestion. Dissolve the final residue in 25 ml of $6M$ hydrochloric acid with magnetic stirring.

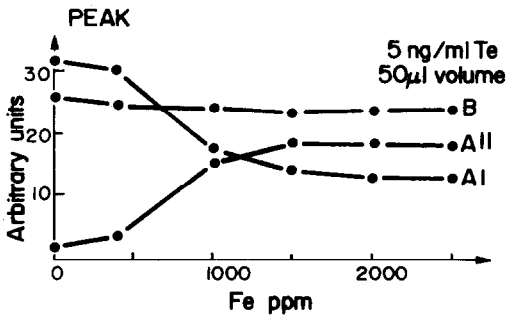

Fig. 1. Effects of varying amounts of iron on the extraction of Te by MIBK. AI and AII: Te recovered in the first and second extractions respectively. B: Te recovered after prior Fe extraction with cupferron–ethyl acetate. Peak height in arbitrary units.

Transfer the solution to a 60-ml separatory funnel, add 4 ml of freshly prepared 4% cupferron solution and 10 ml of ethyl acetate and shake mechanically for 1 min (vigorously for 3–4 min if shaking manually). Transfer the aqueous layer into a beaker and discard the organic layer if analysis for other elements (Sb, Mo, *etc.*) is not required. Put the aqueous solution back in the funnel and complete the Fe extraction by shaking with 5 ml of ethyl acetate. Separate the aqueous layer and shake it for 1 min with 4 ml of MIBK. Transfer the MIBK phase into a 10-ml borosilicate glass bottle and add 1 ml of demineralized water. Gentle shaking by hand is sufficient to concentrate the Te in the aqueous phase. Prepare standards by treating analogously 25 ml of the standard Te solutions. Pipette 25 μl of the aqueous concentrate into the furnace and analyse under the conditions outlined above.

RESULTS

Sensitivity and reproducibility

A very low blank reading was obtained, even with large amounts of iron in the starting solution. A 20-μl sample of 0.2-ppM Te solution (40 pg of Te) gave an absorption reading about twice that of the blank. This value represents the instrumental sensitivity limit for detection of Te and corresponds to a content of 10 ppM Te in the sample

Table 1. Tellurium in reference samples, *ng/g*

Sample	Te found	Literature data* A[2]	B[3]	C[14]
W-1	<10	<90	11	
G-2	<10	<90	5	3.4
				AGV-1
				<10
	2	16		
GSP-1	32–36		31	20
BCR-1	15–25	<90	2	
PCC-1	<10		2	< 8
DTS-1	<10		3	<15
Syenite 2	<10		2	
Sulphide	1200–1350		1490	
GA	<10			
GH	<10			
DR-N	12–15			
BR	10–11			
Fe biotite	12			
T-1	24–29		31	

* A = neutron activation; B = mass spectrometry; C = flameless AAS.

when 0.5 g of sample is used. Instrumental precision was checked by means of a series of replicate readings on 1- and 10-ppM Te aqueous solutions. Good reproducibility (2–3% coefficient of variation) was found for both concentrations.

Standard geological materials

The method has been applied to the analysis of silicate standards for some of which tellurium data had been obtained by techniques such as neutron activation and isotope-dilution mass spectrometry. The results are reported in Table 1. Our data agree sufficiently well with other data for samples which have relatively high Te contents. Unfortunately the Te contents of most of the standards are below the analytical sensitivity achieved with the medium-performance instrument used. A standard sulphide was analysed by dissolving the sample in *aqua regia* and the results are concordant with documented data (Table 1). The method seems to be suitable for microanalysis (1–10 mg of sample) of Te-rich materials such as ore minerals and lunar and meteoritic materials.

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COMPLEXOMETRIC DETERMINATION OF ALUMINIUM IN IRON ORE, SINTER, CONCENTRATES AND AGGLOMERATES

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Summary—A method for the complexometric determination of aluminium in iron ore, sinter, concentrates and agglomerates encountered in international trade is described. The sample is fused in a zirconium crucible with a mixed flux of sodium carbonate and sodium peroxide. The fused mass is completely soluble in hydrochloric acid. The R_2O_3 oxides are then precipitated with ammonia and redissolved in hydrochloric acid. Elements such as iron, titanium and zirconium are separated from aluminium by solvent extraction with cupferron and chloroform. After removal of traces of organic matter from the aqueous phase, the solution is treated with an excess of EDTA, which is then back-titrated with zinc solution (Xylenol Orange as indicator). Addition of ammonium fluoride then releases EDTA equivalent to the aluminium and this is titrated with zinc solution. The method is rapid. The precision and accuracy are excellent, and the results comparable with those obtained by the referee method.

Banerjee and Dutta[1] recently reported a method for determining aluminium in iron ore *etc.* by a complexometric method. The method has the feature of complexing elements such as iron and manganese with mercaptoacetic acid and separating aluminium and titanium as the hydroxides with hexamine. However, titanium interferes and a correction has to be made after determining it colorimetrically. This is time-consuming and complicates the aluminium determination. Any error in the titanium determination will automatically affect the aluminium result. Also, dissolution of the sample is time-consuming and the unattacked residue has to be treated (silica removal, fusion *etc.*) to ensure complete recovery of the aluminium.

Rapid dissolution of iron ore by fusing with sodium carbonate and sodium peroxide in a vitreous carbon crucible[2] completely solubilizes the sample. A method was developed in our laboratory using this rapid sample dissolution and MIBK separation of iron prior to the complexometric determination of aluminium. However titanium interfered. The procedure was therefore modified to incorporate separation of iron, zirconium and titanium by solvent extraction with cupferron and chloroform. (This change permitted the use of the less expensive zirconium crucibles for the dissolution step.) For the subsequent complexometric determination of aluminium the procedure reported earlier[3] was modified, zinc solution being used as titrant in place of lead solution, as the latter sometimes produces opalescence, interfering with the sharpness of the end-point.

EXPERIMENTAL

Apparatus

Zirconium crucibles of 50 ml capacity. Magnetic stirrers with Teflon-coated bars.

Reagents

All reagents are of analytical-reagent grade. Distilled and demineralized water is used throughout.

Ammonium chloride wash solution. A 1% solution containing 2 drops of conc. ammonia solution per 100 ml.

Cupferron. Prepare a fresh 6% solution in water. Filter through a rapid filter. Keep cool (10°C).

Acetate buffer. Dissolve 136 g of sodium acetate trihydrate in about 600 ml of water. Add 7 ml of glacial acetic acid and dilute to one litre. Store in a polyethylene bottle.

Ammonium fluoride solution, 10%. Prepare fresh each day in a polyethylene beaker.

Xylenol Orange indicator. Triturate 0.1 g of Xylenol Orange with a little water to make a paste. Dilute to 100 ml with water. Filter. Store in an amber-coloured glass-stoppered bottle. The solution is stable for one week.

Standard zinc solution, 0.01 *M*. Weigh 0.6538 g of high-purity (99.999%) zinc metal (clippings or small pieces) into a 125-ml Erlenmeyer flask. Add 5 ml of water followed by 2.5 ml of conc. nitric acid. Cover the flask and gently simmer. If the reaction subsides leaving undissolved metal, add 2-ml increments of water followed by simmering until complete solution is obtained. Add 50 ml of water and boil gently for 2 min. Cool. By dropwise addition of 10% sodium hydroxide solution adjust the pH to 4. Dilute to 1 litre with water in a volumetric flask.

EDTA solution, 0.01 *M*. Store in a polyethylene bottle.

Procedure

Transfer 0.50 g of sodium carbonate to a dry zirconium crucible. Add 0.10–0.30 g of accurately weighed (±0.0001 g) iron ore sample (containing 0.001–0.005 g of aluminium), to the crucible, followed by 2 g of sodium peroxide. Mix the contents with a dry stainless-steel spatula. Fuse over a Méker burner (low heat), swirling the crucible until the melt is cherry red and clear. Remove from the heat and swirl until the melt solidifies on the wall of the crucible. Place the crucible in a 250-ml dry beaker. Cool somewhat. Cover with a watch-glass and add about 10 ml of water to the crucible. After effervescence ceases, empty the crucible into the beaker and wash it with about 10 ml of water. Add 10 ml of hydrochloric acid to the crucible and tip it into the beaker. Rinse the crucible with water into the beaker. Dilute to about 70 ml with water. Bring the contents to the boil. Add ammonia solution (1 + 1) dropwise (to raise the pH to 5). Boil for 1 min and immediately filter through a Whatman No. 41 paper, containing some paper pulp. Reserve the beaker. Wash the paper 5 times with hot ammonium chloride wash solution, then 5 times with hot water. Reject the filtrate. Place the reserved beaker under the filter funnel. Dissolve the hydroxide precipitate by adding 5 ml of hydrochloric acid hot dropwise. Wash the filter with nearly boiling hydrochloric acid (1 + 5) until the washings are free from iron. Adjust the volume of the filtrate to 50 ml with hydrochloric acid (1 + 5). Cool to about 10°. Transfer the solution to a cold (10°) 250-ml separatory

funnel. Use 25 ml of cold water (10°) for rinsing the beaker into the separatory funnel. Add 20 ml of cold freshly prepared and filtered cupferron solution. Mix slightly. Add 20 ml of chloroform. Shake vigorously for 1 min. Let the layers separate. Draw off the lower organic layer. Add 5 ml of chloroform to the separatory funnel to displace the cupferronates on the surface of the aqueous layer. Draw off the organic layer. Treat further with cupferron and chloroform as shown in the following table (commensurate with the sample weight).

Sample, *g*	Cupferron, *ml*	Chloroform, *ml*	Cupferron, *ml*	Chloroform, *ml*
0.3	20	20	15	20
0.2	15	20	—	—
0.1	10	20	—	—

Finally add two successive 20-ml portions of chloroform to the aqueous phase, shaking vigorously for 1 min. Let settle and separate. Draw off the organic layer. Wipe the stem of the separatory funnel with a filter paper wick. Drain the aqueous phase into a 250-ml beaker, rinsing with 5 ml of hydrochloric acid (1 + 5). Boil for a few minutes. Remove from the heat. Add 5 ml of conc. nitric acid and 10 ml of perchloric acid. Cover with a ribbed cover-glass. Evaporate nearly to dryness. Remove from the heat. Add 10 ml of hydrochloric acid (1 + 1). Heat to dissolve the salts and then add 50 ml of water and bring to the boil. Filter through a Whatman No. 41 paper and wash several times with hot water. Cool. Add an excess of 0.01*M* EDTA (25 ml is sufficient) by pipette. Adjust the pH to 4 (using a pH-meter) by dropwise addition first of 10% sodium hydroxide solution till the pH reaches 2.5 and then of 1% sodium hydroxide solution. Dilute to 100 ml with water. Cover the beaker and bring to the boil. Keep boiling gently for 10 min. Cool. Add 15 ml of acetate buffer and 7 drops of Xylenol Orange indicator. Stir with the magnetic stirrer and titrate with 0.01*M* zinc solution. The colour changes to a persistent (30 sec) pink at end-point. Add 10 ml of ammonium fluoride solution. Boil gently for 10 min, cool and titrate the liberated EDTA with 0.01*M* zinc solution as before.

$$\%\text{Al} = \frac{0.02698\,T}{\text{sample weight (g)}}$$

where T is the volume of zinc solution used in the second back-titration.

RESULTS AND DISCUSSION

An earlier method developed by the author had been submitted to round-robin testing to determine its suitability as a standard complexometric procedure, on behalf of ISO (International Standard Organization). The principle was as follows. The sample was fused in a vitreous carbon crucible with a mixed flux of sodium carbonate and sodium peroxide and the fused mass was completely dissolved in dilute hydrochloric acid. After dehydration of the silica, iron was removed from the filtrate by MIBK extraction. The residual organic matter in the aqueous phase was destroyed and aluminium along with other "R_2O_3" oxides was precipitated with ammonia and redissolved. The solution was then treated with an excess of EDTA. The excess of EDTA was titrated with standard lead solution, with Xylenol Orange as indicator. Addition of ammonium fluoride released the EDTA bound to aluminium, and this EDTA was titrated with lead solution. Statistical evaluation of the results obtained showed both the precision and accuracy to be satisfactory, but concern was expressed about the possibility of interference from titanium, which is a constituent of some ores on the international market.

Table 1. Comparison of aluminium results (Al, %)

Sample	Assigned value†	Vitreous carbon‡		Present method
		n	$\bar{x}$	
1. Marcona	0.35	64	0.369	0.35_1, 0.36_2, 0.36_1
2. Krivoj	0.66	66	0.671	0.67_4, 0.67_4, 0.67_4
3. Sinter BCS 377	1.80	66	1.803	1.76_8, 1.78_5, 1.77_0
4. Minette	2.38	60	2.430	2.35_3, 2.36_1, 2.42_4, 2.35_3
5. Sinter BCS303	3.53	66	3.561	3.50_3, 3.50_9, 3.48_7
6. Phillipine iron sand*	1.43	—	—	1.42_5, 1.43_0, 1.44_4, 1.42_5

* Contains 3.6% Ti.

† Assigned by ISO after the international round-robin testing of the aluminium oxinate gravimetric method.

‡ ISO round-robin tests—earlier complexometric method (*n* is the number of replicates and $\bar{x}$ is the arithmetic mean).

Table 2. Approximate composition of iron ore samples (%)

Ore, origin	Fe	SiO_2	CaO	MgO	Al_2O_3	TiO_2	P	S	Mn	As	V	F
Marcona	63	5.4	1.4	1.9	0.8	0.06	0.04	1.2	0.03			
Krivoy	48	28	0.9	0.2	1.1	0.04	0.05	0.03	0.03	0.002	0.003	
Sinter BCS 377	52.5	8.6	10.8	1.1	3.40	0.19	0.31	0.083	0.50			
Minette	32	9	16	2	4	0.2	0.7	0.1	0.2	0.02		
Sinter BCS 303	36	17	20	2	7	0.3	0.5	0.2	1			
Phillippine iron sand	60	2	0.7	2	3	6	0.1	0.01	0.6	0.003	0.3	0.01

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Accordingly additional investigations were carried out in our laboratory to obviate titanium interference and simplify the method. Dehydration of silica after sample dissolution was found to be unnecessary and was dropped. Precipitation of hydroxides after the sample dissolution eliminated the unwanted sodium salt (used for fusing the sample). The precipitate containing both aluminium and titanium was redissolved in hydrochloric acid. The acidity was adjusted to about 2 *M* in hydrochloric acid for direct separation of interfering elements such as iron, titanium and zirconium, by extraction into cupferron–chloroform. The number of cupferron extractions was based on the sample weight as described in the procedure. Removal of zirconium from the solution permitted the use of a zirconium crucible in place of the more expensive and consumable vitreous carbon crucible.[2]

The complexometric finish for aluminium was slightly modified by replacing lead with zinc solution for titrating the EDTA. This modification eliminated the opalescence experienced with the hydrolysis of lead noticeable around pH 6, which affects the sharpness at the equivalence point. No such problem is encountered with zinc as titrant.

Table 1 summarizes the results, showing the comparison between values obtained by using vitreous carbon (earlier round-robin testing) and zirconium (present method) crucibles. Inclusion of the Phillipine Iron Sand sample (containing 3.6% titanium) in this study demonstrates that the method is entirely free from titanium interference. The results are compared with those assigned by the ISO after international round-robin testing of the tedious aluminium oxinate gravimetric method. The wide range of composition of the samples selected for this study (Table 2) illustrates the universal applicability of the method. The procedure described is rapid, simple, precise, accurate and suitable for referee analysis.

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SIMULTANEOUS DETERMINATION OF OXYGEN AND MERCURY IN INORGANIC AND ORGANIC MERCURY COMPOUNDS

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Summary—Oxygen and mercury in inorganic and organic mercury compounds are determined simultaneously by a modification of the Schütze–Unterzaucher method. The determination of mercury is not influenced by the presence of sulphur and nitrogen in the samples. In 13 inorganic and organic mercury compounds, oxygen has been determined with an error of less than 0.4% and mercury with an error of less than 0.5%.

Methods for analysis of inorganic and organic mercury compounds for mercury have been reported by Onoe,[1] Pechanec and Horáček,[2] and Gouverneur and Hoedeman,[3] and for mercury and halogen simultaneously, by Pechanec,[4] Marzadro and Zavattiero,[5] and Jerie.[6] Pechanec and Horáček[7,8] and Gel'man[9] have reported methods for simultaneous determination of carbon, hydrogen and mercury, and Korshun *et al.*[10] have reported simultaneous determination of these three elements and halogen.

We have already reported determination of oxygen in inorganic and organic mercury compounds,[11] but no methods have been introduced, until now, for simultaneous determination of oxygen and mercury in such compounds. The present study was designed for this simultaneous determination.

EXPERIMENTAL

Samples

The samples used were compounds of which the carbon and hydrogen contents had been confirmed analytically.

Reagents

The reagents used were the same as those in our previous paper.[12]

Apparatus

An absorption tube for mercury was attached to the exit end of a pyrolysis tube. An enlarged figure of the attachment is shown in Fig. 1. The method for oxygen determination was the same as in the previous paper. For mercury determination the mercury absorption tube was disconnected from the apparatus 30 min after the start of pyrolysis and weighed, and the weight of mercury collected was corrected for the blank.

RESULTS AND DISCUSSION

Temperature of the sample heater

For determination of oxygen in inorganic and organic mercury compounds, the temperature of the sample heater must be higher than that needed for pyrolysis of mercury oxides to give oxygen. Temperatures over 500 were found to suffice for determination of oxygen in mercury (II) oxide. Therefore 900 was considered sufficiently high for determination of oxygen in organic compounds and was employed as the temperature of the sample heater.

Temperature of the inlet of the mercury absorption tube

Absorption of mercury vapour by porous silver was first carried out in 1960 by Imaeda *et al.*,[13] and later by Mitsui *et al.*[14] A large quantity of mercury is known to be evaporated at 80–85 . In our tests, about 90 was found to be high enough for the temperature of the inlet of the mercury absorption tube.

Influence of other elements

The influence of sulphur and nitrogen in the sample was investigated, and favourable results were obtained when mercury was determined in mercury(II) cyanide, sulphide or thiocyanate.

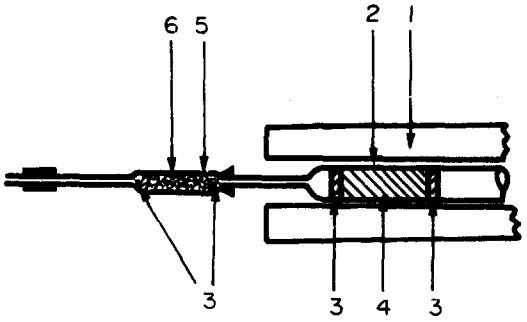

Fig. 1.

Simultaneous determination of oxygen and mercury

By the procedure previously described,[12] oxygen and mercury in inorganic and organic mercury compounds were simultaneously determined. As shown in Table 1, quite good results were obtained: oxygen could be determined with an error of less than 0.4%, and mercury with an error of less than 0.5%.

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Table 1. Simultaneous determination of oxygen and mercury in inorganic and organic mercury compounds

Sample	Sample taken, *mg*	Oxygen			Mercury		
		CO_2, *mg*	Found, %	Calcd., %	Hg, *mg*	Found, %	Calcd., %
Mercury(I) acetate CH_3COOHg	3.283 3.947 3.446	1.114 1.354 1.162	12.3_4 12.4_7 12.2_6	12.32	2.546 3.046 2.669	77.6 77.2 77.5	77.25
Mercury(I) citrate $C_6H_5O_7Hg_3$	3.806 3.305 3.250	1.497 1.281 1.281	14.3_0 14.0_9 14.3_3	14.16	2.898 2.520 2.475	76.1 76.3 76.2	76.09
Mercury(I) nitrate $HgNO_3 \cdot H_2O$	3.180 3.987 3.193	1.963 2.487 1.989	22.4_4 22.6_8 22.6_5	22.81	2.272 2.853 2.273	71.5 71.6 71.2	71.48
Mercury(I) sulphate Hg_2SO_4	3.272 3.180 3.522	1.132 1.131 1.230	12.5_8 12.9_3 12.7_0	12.87	2.638 2.566 2.825	80.6 80.7 80.2	80.68
Mercury(II) acetate $(CH_3COO)_2Hg$	3.408 3.333 4.680	1.891 1.832 2.624	20.1_8 19.9_9 20.3_9	20.08	2.143 2.103 2.937	62.9 63.1 62.8	62.94
Mercury(II) oxide (red) HgO	3.178 3.413 3.430	0.654 0.707 0.676	7.4_8 7.5_3 7.1_7	7.39	2.943 3.160 2.170	92.6 92.6 92.4	92.61
Mercury(II) oxide (yellow) HgO	3.715 3.235 4.071	0.757 0.680 0.804	7.4_1 7.6_4 7.1_8	7.39	3.447 3.004 3.765	92.8 92.9 92.5	92.61
Mercury(II) sulphate $HgSO_4$	3.615 3.682 3.031	2.117 2.187 1.811	21.2_9 21.6_0 21.7_2	21.57	2.457 2.471 2.045	68.0 67.1 67.5	67.61
2,5-Bis [(acetoxymercuri)methyl]-1,4-dioxan $C_{10}H_{16}O_6Hg_2$	3.818 3.950 3.215	1.101 1.652 1.356	15.2_5 15.2_1 15.3_4	15.16	2.424 2.500 2.044	63.5 63.3 63.6	63.34
(*o*-Carboxyphenylthio)ethylmercury(II) $C_9H_{10}O_2SHg$	4.594 3.448 3.593	1.066 0.816 0.822	8.4_4 8.6_0 8.3_2	8.36	2.395 1.814 1.881	52.1 52.6 52.4	52.40
[(5-Carboxybenzoxazol-2-yl)thio]-ethylmercury(II) $C_{10}H_9NO_3SHg$	3.680 3.756 4.138	1.119 1.209 1.318	11.0_6 11.7_0 11.5_8	11.33	1.750 1.790 1.952	47.6 47.7 47.2	47.33
Phenylmercury(II) acetate $C_6H_5HgOOCCH_3$	4.162 3.370 3.208	1.103 0.885 0.848	9.6_4 9.5_5 9.6_1	9.50	2.494 2.015 1.901	59.9 59.8 59.3	59.57
Phenylmercury(II) nitrate (base) $C_6H_5HgOH \cdot C_6H_5HgNO_3$	4.520 3.969 3.551	1.257 1.120 1.006	10.1_1 10.2_6 10.3_0	10.09	2.863 2.505 2.252	63.3 63.1 63.4	63.24

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CATALYTIC EFFECT OF COPPER ON THE HEXACYANOFERRATE(III)–CYANIDE REDOX REACTION—II*

CATALYTIC DETERMINATION OF COPPER

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Summary—A catalytic method for the determination of copper, based on the catalysis of the hexacyanoferrate(III)–cyanide redox reaction, is proposed. Experimental conditions to achieve the lowest detection limit are selected from the kinetics of both the catalysed and the uncatalysed reactions. The experimental measurements can be made at room temperature without close control. The rate-constant method is the most sensitive and precise, whereas the fixed-concentration and fixed-time methods appear to be the most rapid for routine analysis. A detection limit of 1.3 ng/ml and a coefficient of variation of about 3% for the determination of 63 ng/ml can be achieved. The catalytic effect of copper seems to be highly specific. Lead(II), bismuth (III), antimony (III), iron (II), iron(III), chromium(III), lanthanum(III), cerium(III), titanium(IV), zirconium(IV) and uranium(VI) interfere by precipitation. Species such as tin(II), cobalt(II), manganese(II), sulphite and thiosulphite cause serious interference because they react with hexacyanoferrate(III). Chromate interferes by its colour. Suitable methods to avoid the interferences from antimony(III), iron(III), chromium(III), titanium(IV), zirconium(IV), uranium(VI) and chromate are proposed.

The catalytic effect of copper on many homogeneous redox reactions has been frequently applied to the catalytic determination of copper at trace levels,[1–4] with detection limits in the range $1–10^{-4}$ μg/ml.

The hexacyanoferrate(III) oxidation of cyanide is copper-catalysed[5] and a kinetic study has been reported,[6] along with mechanisms for the catalysed and uncatalysed reactions. This paper reports the analytical application of the reaction.

EXPERIMENTAL

Procedure for the determination of copper

Transfer by pipette 1.0 ml of 0.5*M* sodium cyanide and 40.0 ml of 5.0*M* sodium chloride into a series of 50-ml standard flasks. Add 0–4 ml of 10^{-5}*M* copper nitrate standard solution from a microburette. Finally, add by pipette 5.0 ml of 5.0×10^{-3}*M* potassium hexacyanoferrate(III) solution (the reaction starts at this instant), shake and make up quickly to 50 ml with distilled water. Although it is unnecessary to use a thermostat, care must be taken that all the solutions are at room temperature (a range of ±2° can be allowed without a significant loss of precision). Measure the absorbance at 422 nm in a 10-mm spectrophotometric cell and plot (*a*) the reciprocal of the time elapsed for the absorbance to decrease to 0.400 or (*b*) the absorbance measured after 5 min from the start of reaction, against copper concentration. Should a larger precision and/or sensitivity be required, the more laborious rate-constant method can be followed: record the kinetic curves during about 50 min, plot the reciprocal of absorbance *vs.* time, and plot the slope of the straight portion of the lines *vs.* copper concentration. Handle the sample in the same way and determine the unknown copper concentration from the calibration graph.

RESULTS AND DISCUSSION

Selection of optimum conditions

To achieve the maximum sensitivity (minimum detection limit) the working conditions must be chosen so that the ratio of the catalysed and uncatalysed reaction rates (k^c_{exp}/k_{exp}) is as large as possible.

Because the uncatalysed reaction is first-order with respect to cyanide but the rate of the catalysed reaction is independent of cyanide concentration the sensitivity will be increased by decreasing the concentration of cyanide. However, the cyanide concentration must be high enough to remain essentially constant during the reaction [*i.e.*, at least 50 times the hexacyanoferrate(III) concentration]. The hexacyanoferrate(III) side-reaction which takes place with first-order dependence on the hydroxide ion is not catalysed by copper and therefore the pH must not be too high and should be only that of the cyanide medium.

The effects of $Fe(CN)_6^{3-}$ concentration, $Fe(CN)_6^{4-}$ concentration and ionic strength on the k^c_{exp}/k_{exp} ratio are shown in Table 1. As can be seen, hexacyanoferrate(III)

Table 1. Selection of optimum conditions

$[Fe(CN)_6^{3-}]$, $M \times 10^4$	k^c_{exp}/k_{exp}	$[Fe(CN)_6^{4-}]$, $M \times 10^3$	k^c_{exp}/k_{exp}	I	k^c_{exp}/k_{exp}
1.0	1.0	1.4	1.2	1.0	0.24
3.0	2.0	2.0	1.1	2.0	0.38
5.0	2.2	3.3	0.9	2.5	0.47
7.0	2.0	10.0	0.6	3.0	0.52
9.0	2.1			4.0	0.64

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concentrations higher than $3.0 \times 10^{-4} M$ do not influence the ratio but an increase in the hexacyanoferrate(II) concentration decreases the ratio. Consequently, hexacyanoferrate(II) must be absent in the initial solution. On the other hand, the advantage of working at ionic strength as high as possible is evident from the k^c_{exp}/k_{exp} values obtained at different ionic strengths.

Application of the Arrhenius equation to the rate constants of the uncatalysed and catalysed reactions gives the expression:

$$\frac{k^c_{exp}}{k_{exp}} = a \exp - \left[\frac{E^c_a - E_a}{RT}\right]$$

where a is the quotient of the pre-exponential factors of the catalysed and uncatalysed reactions and E^c_a and E_a are the respective activation energies. The k^c_{exp}/k_{exp} ratio increases with temperature since, in this case, $E^c_a > E_a$. However, $E^c_a - E_a$ is small (1.0 kcal/mole) and so the relative increase in the k^c_{exp}/k_{exp} ratio is only about 0.6% per degree. Consequently, increasing the temperature does not alter the sensitivity very much. However, because of the low temperature coefficient of the reaction, temperature control is unnecessary and it is possible to work at room temperature.

The best experimental conditions for the catalytic determination of copper, from the considerations above, are: $K_3Fe(CN)_6$ $5.0 \times 10^{-4} M$; NaCN $0.01 M$; NaCl $4.0 M$ and T about 20° (±2–3°).

Calibration graph and sensitivity

Four methods can be used in catalytic analysis to obtain the calibration graph: the fixed-concentration, fixed-time, initial-rate and rate-constant methods. The best method for our reaction was chosen on criteria of sensitivity and precision. The sensitivity of an analytical procedure can be expressed as the detection limit. The statistical detection limit P defined by Kaiser[7] can be calculated from the standard deviation (s_0) of the background signal (P_0):

$$P = P_0 + 3\sqrt{2}\, s_0.$$

The standard deviation for the background signal was calculated from ten separate kinetic curves for the uncatalysed reaction, obtained under optimum experimental conditions. Precision was evaluated from the coefficient of variation calculated for the $10^{-6} M$ level of copper concentration (63 ng/ml).

Fixed-concentration method. If the $Fe(CN)_6^{3-}$ concentration (or the absorbance) is fixed near to its initial value, a first-order dependence on $Fe(CN)_6^{3-}$ can be assumed and the following equation derived for the calibration curve:

$$1/t = mk_1 + mk^c_1[Cu]$$

where m is $\ln[FeCN)_6^{3-}]_f/[Fe(CN)_6^{3-}]_0$ and k_1 and k^c_1 are the rate constants for the uncatalysed and the catalysed reaction, respectively. The reciprocal of the time needed for the absorbance to decrease to 0.400 (about 80% of its theoretical initial value) was plotted *vs.* copper concentration in the range $1–8 \times 10^{-7} M$. This calibration graph was linear. A detection limit of 2.8 ng/ml was obtained and the coefficient of variation was about 6%.

Fixed-time method. When the time is fixed low enough for the reaction to proceed to a low extent, the following expression is derived from the first-order rate equation:

$$A = A_0 - k_1 t_f A_0 - k^c_1\, t_f\, A_0[Cu]$$

where A_0 and A are the absorbance values at times zero and t_f respectively. By plotting the absorbance values measured at $t = 5$ min *vs.* copper concentration in the range $0.1–1 \times 10^{-7} M$ (differential fixed-time method), an almost linear curve was obtained, from which a detection limit of 4.4 ng/ml and a coefficient of variation of about 4% were calculated. A lower detection limit can be attained for larger fixed times (2.2 ng/ml at $t = 50$ min), but the curve is not linear and the method becomes less precise (the coefficient of variation is about 7%). After the initial period, a second-order relation is satisfied for the reaction and the following equation can be deduced:

$$\frac{1}{A} = \frac{1}{A_0} + \frac{k_2 t_f}{\epsilon} + \frac{k^c_2 t_f [Cu]}{\epsilon}$$

where ϵ is the molar absorptivity of hexacyanoferrate(III).

By plotting the reciprocal of absorbance at $t = 50$ min *vs.* copper concentration (second-order integral fixed-time method), a linear curve was obtained in the range $1–40 \times 10^{-7} M$, although the detection limit and the coefficient of variation were somewhat larger (5 ng/ml and 9%).

Initial-rate method. The initial rate may be measured as $\Delta A/\Delta t$ at low Δt. The pseudo first-order equation gives the initial rate for the overall reaction as:

$$-\Delta A/\Delta t = k_1 A_0 + k^c_1 A_0[Cu]$$

A plot of the initial ($\Delta A/\Delta t$) values *vs.* copper concentration yields the initial-rate calibration graph (differential-tangents method). The curve obtained was essentially linear for copper below $10^{-6} M$. A detection limit of 5.7 ng/ml and a coefficient of variation of about 6% were calculated.

Rate-constant method. The total pseudo second-order rate constant varies with the catalyst concentration according to the equation:

$$k_{tot} = k_2 + k^c_2[Cu].$$

A linear range up to $4 \times 10^{-6} M$ copper could be achieved by plotting the pseudo second-order rate constant *vs.* copper concentration (rate-constant or integral-tangents method). The detection limit could be improved (1.3 ng/ml) and the precision of the method was also better (3%).

It can be inferred from the results above that the rate-constant method yields both maximum sensitivity and precision, although it is the most time-consuming. On the other hand, the variable-time, fixed-time and initial-rate methods appear to be sensitive, precise and rapid enough to be useful for routine analysis.

Effect of foreign ions

The effect of 47 cations and anions on the determination of a 63 ng/ml concentration of copper was studied. The following metal ions do not interfere at the 100 μg/ml level (higher levels were not tested): silver, thallium(I), mercury(II), cadmium, arsenic(III), molybdenum(VI), tungsten(VI), vanadium(V), aluminium, nickel, zinc, calcium, strontium, barium, potassium and ammonium. Lead, bismuth, antimony(III), iron(II), iron(III), chromium(III), lanthanum, cerium(III), titanium(IV), zirconium and uranium(VI) give precipitates in the reaction medium. Tin(II) is precipitated as the hydroxide and readily reduces the hexacyanoferrate(III). Cobalt(II) and manganese(II) form cyanide complexes which also reduce hexacyanoferrate(III). Lead, bismuth, tin(II), antimony(III), iron(II), chromium(III), lanthanum, cerium(III), titanium(IV), zirconium, uranium(VI) and cobalt(II) do not interfere at concentrations of 10 μg/ml. Iron(III) and manganese(II) do not interfere at the 1 μg/ml level. The precipitation of antimony(III), iron(III), chromium(III), titanium(IV), zirconium, uranium(VI) and tin(II) can be avoided by using $0.01 M$ sodium tartrate medium. Antimony(III), titanium(VI) and zirconium tartrate complexes are colourless and do not interfere. Iron(III), chromium(III) and uranium(VI) at higher concentrations give coloured tartrate complexes which interfere in the spectrophotometric measurement of the hexacyanoferrate(III) concentration, but can be compensated for by using a test solution [with-

out the hexacyanoferrate(III)] as reference in the absorbance measurements. Tin(II), however, although forming a soluble tartrate complex, still interferes owing to its reducing properties.

Carbonate, fluoride, oxalate, tartrate, citrate, phosphate, iodate, sulphate, bromide, iodide, acetate, nitrate, chlorate and bromate do not interfere at the 500 μg/ml level. Sulphite and thiosulphate readily reduce hexacyanoferrate(III). Chromate interferes owing to its colour, but this can easily be compensated for by using as reference a test solution with the hexacyanoferrate(III) omitted. None of these three anions causes appreciable interference at the 10 μg/ml level.

The only interferences are caused by precipitation, redox or colour side-reactions. None of the foreign ions studied acts as a catalyst or an inhibitor. The absence of inhibitors can be attributed to the great stability of the copper(I)–cyanide complexes.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XXVIII*

NEW METHOD FOR SUCCESSIVE DETERMINATION OF CALCIUM AND MAGNESIUM

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Summary—A new method for successive determination of calcium and magnesium is proposed. It is based on the indirect determination of calcium in borax media by back-titration of excess of EGTA with lead nitrate. Magnesium is then determined in ammonia buffer with DCTA. For both titrations Thymolphthalexone is used as indicator. The exceptional role of DCTA in direct titration of magnesium is established experimentally and explained.

In a previous communication[1] we described a simple method for the determination of calcium in the presence of large amounts of magnesium. The method is based on back-titration of excess of EGTA with zinc solution, with Thymolphthalexone as indicator. At the end-point the first small excess of zinc ions displaces magnesium from its indicator complex and the original blue colour of the solution disappears:

$$\underset{\text{blue}}{Mg_2In^{2-}} + 2\,Zn^{2+} = \underset{\text{colourless}}{Zn_2In^{2-}} + 2\,Mg^{2+} \qquad (1)$$

The titrations are performed in borax solution, which prevents precipitation of magnesium as the hydroxide. Similarly we can determine the sum of calcium and manganese in the presence of magnesium, and manganese can be determined selectively after the masking of calcium and magnesium with ammonium fluoride (the well-known disadvantage of which—co-precipitation of manganese on precipitated calcium fluoride—can be eliminated as described later by us).[2] This method was used for determination of only the calcium, in the presence of large amounts of magnesium up to 100–200 mg. Such quantities of magnesium are inconvenient for subsequent determination, because of high consumption of titrant (100 mg of Mg = 82.23 ml of 0.05*M* EDTA), though accurate results should be obtained. We therefore turned our attention to concentration ratios which are suitable for reliable determinations of both the calcium and the magnesium. We assume that the limiting molar ratios of Ca:Mg are 10:1 or 1:10 (weight ratios 16:1 and 1:6).

Our preliminary experiments have shown that after the determination of calcium as above (back-titration of excess of EGTA with zinc), the indicator remains blocked in ammonia buffer and the solutions stay colourless even in the presence of a large concentration of magnesium. Such a solution gives a distinct colour reaction with Eriochrome Black T, but attempts to use this indicator for titration with EDTA or DCTA failed, the results always being too high because of the co-titration of the zinc bound by EGTA:

$$Zn\text{–}EGTA + EDTA = Zn\text{–}EDTA + EGTA \qquad (2)$$
$$\log K = 12.8 \qquad \log K = 16.5$$
$$Zn\text{–}EGTA + DCTA = Zn\text{–}DCTA = EGTA \qquad (3)$$
$$\log K = 12.8 \qquad \log K = 18.0$$

In addition, the liberated EGTA obscured the end-point, by forming a relatively weak complex with magnesium (log $K = 5.2$).

After these unsuccessful experiments we chose lead nitrate for titration of the excess of EGTA. Lead behaves similarly to zinc, forming the practically colourless complex Pb_2In^{2-} with the indicator. In the titration of EGTA the first traces of excess of lead decolorize the blue solution of the Mg_2In^{2-} complex. Such an indirect determination of calcium is found to have the same accuracy as the similar titration with zinc, described previously.[1] For the direct determination of the remaining magnesium with EDTA or DCTA we have to consider the following exchange reactions:

$$Pb\text{–}EGTA + EDTA = Pb\text{–}EDTA + EGTA \qquad (4)$$
$$\log K = 13 \qquad \log K = 18.0$$
$$Pb\text{–}EGTA + DCTA = Pb\text{–}DCTA + EGTA \qquad (5)$$
$$\log K = 13 \qquad \log K = 19.7$$

We can expect the same effects as for zinc in the titration of magnesium in presence of the Pb–EGTA complex. The titration of magnesium with EDTA and Eriochrome Black T was indeed not successful because of co-titration of lead according to equation (4), but we obtained very good results for titration of magnesium with DCTA. This finding is at first sight astonishing, even though it is known that the formation of complexes with DCTA proceeds a little

* Part XXVII—*Talanta*, 1977, **24**, 645.

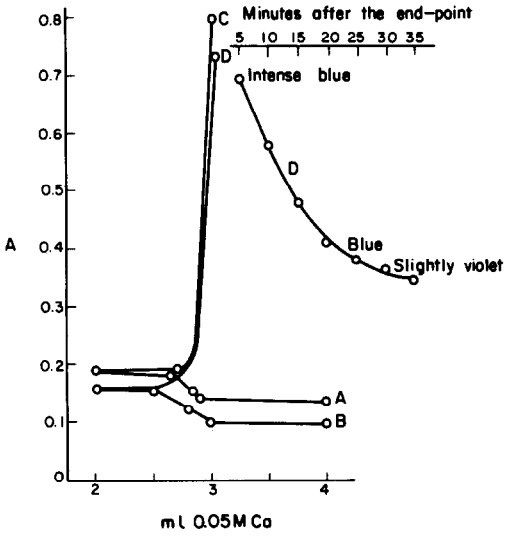

Fig. 1. Titration of EGTA and EDTA (DCTA) with 0.05*M* calcium chloride in the presence of 2 ml of 0.05*M* lead solution. All solutions contained, in 100 ml, 2 ml of ammonia buffer, 5 ml of conc. ammonia solution and 1 ml of freshly prepared 0.1% Thymolphthalexone solution. All measurements were made in 3-cm cuvettes, the whole spectrum being recorded and the maximum absorbance at 620 nm noted. After the end-point was reached the absorbance was measured during 5–35 min. A: 2 ml of 0.05*M* Pb + 5 ml of 0.05*M* EGTA. B: 2 ml of 0.05*M* Pb + 2.5 ml of 0.05*M* EGTA + 2.5 ml of 0.05*M* DCTA. C: 2 ml of 0.05*M* Pb + 2.5 ml of 0.05*M* EGTA + 2.5 ml of 0.05*M* EDTA. D: 2 ml of 0.05*M* Pb + 5 ml of 0.05*M* EDTA.

more slowly than with EDTA. We would expect reaction (5) to proceed quantitatively because of the large difference between the stability constants of the complexes.

From the analytical point of view it was important to know whether reaction (5) occurred either to a certain extent or not at all. The following experiments were done. A mixture of 2 ml of 0.05*M* lead nitrate and 2.5 ml of 0.05*M* EGTA was diluted to about 50 ml with redistilled water, and 2 ml of ammonia buffer, 5 ml of conc. ammonia solution, 1 ml of freshly prepared 0.1% Thymolphthalexone solution and 2.5 ml of 0.05*M* DCTA (equivalent to the EGTA and in 20% excess relative to Pb) were added. The solution was diluted to 100 ml and titrated with 0.05*M* calcium chloride spectrophotometrically.

During the titration of the free EGTA and DCTA the absorbance did not increase even if we overtitrated with calcium (see curve B in Fig. 1). Similar behaviour was shown by a solution containing only lead (2.0 ml of 0.05*M* solution) and 5 ml of 0.05*M* EGTA (see curve A in Fig. 1). In both cases the detection of the end-point fails because the first traces of displaced lead immediately block the indicator, preventing its colour reaction with calcium.

When the DCTA is replaced by 2.5 ml of 0.05*M* EDTA the end-point of the titration with calcium is given by the appearance of the intense blue colour of the calcium–indicator complex and the absorbance increases considerably (curve C in Fig. 1).

These experiments prove that DCTA does not react at all with the Pb–EGTA complex under our experimental conditions. On the other hand EDTA reacts with this complex quantitatively according to equation (4). On the basis of this we were able to develop a simple method for successive determination of calcium and magnesium.

Procedure

To the slightly acidic solution containing 1–20 mg of Ca and 0.5–30 mg of Mg add enough 0.05*M* EGTA to complex the whole of the calcium (1 ml of EGTA ~ 2 mg of Ca), and 10–20% in excess. Then add 10–15 ml of saturated borax solution and small amount of indicator (1:100 dry mixture of Thymolphthalexone and KCl) and dilute to 100 ml. Titrate the slightly blue solution with 0.05*M* lead nitrate. During the titration the blue colour becomes progressively deeper up to the end-point. At the end-point the solution becomes colourless. The consumption of EGTA corresponds to the amount of calcium. Then add to the colourless solution 1 or 2 drops of EGTA. After a few seconds the blue colour of the solution reappears. Add 10–15 ml of conc. ammonia solution and titrate the magnesium with 0.05*M* DCTA, from intense blue to colourless.

The method can be modified very simply. After the titration of calcium we can leave the indicator blocked, add Eriochrome Black T and ammonia buffer, and titrate with 0.05*M* DCTA from red to blue. Some results of the determination of calcium and magnesium in synthetic mixtures are presented in Table 1.

This method is more convenient than our method developed some years ago, which was the first to use the combination of EGTA (for Ca) and DCTA (for Mg). The older method needs at least two aliquots of sample solution and careful maintenance of the analytical conditions. In addition the present method eliminates the interference of excessive EGTA.

It is difficult to explain the difference in rate between reactions (4) and (5). Margerum *et al.*[5] studied the displacement of DCTA from its metal complexes by lead or copper and explained its slowness in terms of the rigidity of the metal–DCTA complex imposed by the cyclohexane ring, which reduces the flexibility of the ligand groups. In our case we must turn this argument round, and suggest that because of the relative rigidity of the free DCTA in comparison with free EDTA, there is an orientation factor in

Table 1. Determination of calcium with EGTA and magnesium with DCTA

Taken		Back-titration,		Found	Direct titration	Found
Ca (0.05*M*), *ml*	Mg (0.05*M*), *ml*	EGTA (0.05*M*), *ml*	Pb (0.05*M*), *ml*	Ca (0.05*M*), *ml*	DCTA (0.05*M*), *ml*	Mg (0.05*M*), *ml*
3.13	2.94	8.20	5.09	3.11	3.02	3.02
		8.20	5.08	3.12	2.98	2.98
1.04	2.94	4.00	2.99	1.01	3.00	3.00
6.25	0.49	9.00	2.76	6.24	0.42	0.42
0.52	8.33	4.00	3.47	0.53	8.50	8.50
0.52	9.80	4.00	3.42	0.58	9.85	9.85
0.52	24.50	5.00	4.49	0.51	24.48	24.48

the kinetics of the system so that although the DCTA reaction is thermodynamically the more favourable, kinetic factors prevent its occurrence in the time needed to perform the titration. We may mention in support of this argument (which we advance only as a suggestion) that the difference in stability between the DCTA and EDTA complexes of the same metal ion is often attributed to the entropy change for formation of the EDTA complex, being lower because there is loss of translational and rotational entropy when the >CH–CH< bond of the EDTA becomes "anchored", a situation that does not arise with DCTA because the bond is already incapable of rotation.

Indirect determination of magnesium

If for some reason we wish to use only EGTA and EDTA for such determinations we have to modify the method as follows.

Procedure. After the determination of calcium, we add to the colourless solution an excess of 0.05*M* EDTA to complex the whole of the calcium and all the lead bound to EGTA, then 10–15 ml of conc. ammonia solution, and titrate with 0.05*M* calcium chloride from colourless to intense blue. The excess of EDTA for complexing all the calcium and lead (and magnesium) is necessary because reaction (4) must be quantitative. Otherwise the last remaining traces of Pb–EGTA complex (which is the weakest) react with calcium and the liberated lead immediately blocks the indicator (see curve *B* in Fig. 1). The blue colour at the end-point is stable for at least 5–10 min and then fades slowly because of displacement of lead from the Pb–EDTA complex by calcium. In visual titrations the colour change is very sharp. The fading of the blue colour can be followed spectrophotometrically (see curve *D*, Fig. 1). For such a titration of magnesium we cannot use DCTA at all, because it does not react quantitatively with the Pb–EGTA complex even if present in excess.

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INFLUENCE OF THE SOLVENT MEDIUM ON FORMATION OF Cu(II), Zn(II) AND Ni(II) HEXACYANOCOBALTATES*

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Summary—Investigations on precipitation of metal hexacyanocobaltates from mixed solvent media have confirmed the earlier interpretation of the mechanism and provided further insight into it.

In an earlier investigation[1] we studied the formation of insoluble compounds between $K_3Co(CN)_6$ and various metal ions in aqueous medium, with the purpose of identifying the reaction stoichiometry for various concentrations of the reacting species and order of addition, to verify and complete the data reported in the literature.[2–8] The results were interpreted as implying a precipitation reaction in 1:1 ratio between the ion-pair[9] K^+–$Co(CN)_6^{3-}$ and the cation, any further transformation then occurring in the solid phase.

Since the equilibrium constant of ion-pair formation increases with decreasing dielectric constant of the solvent

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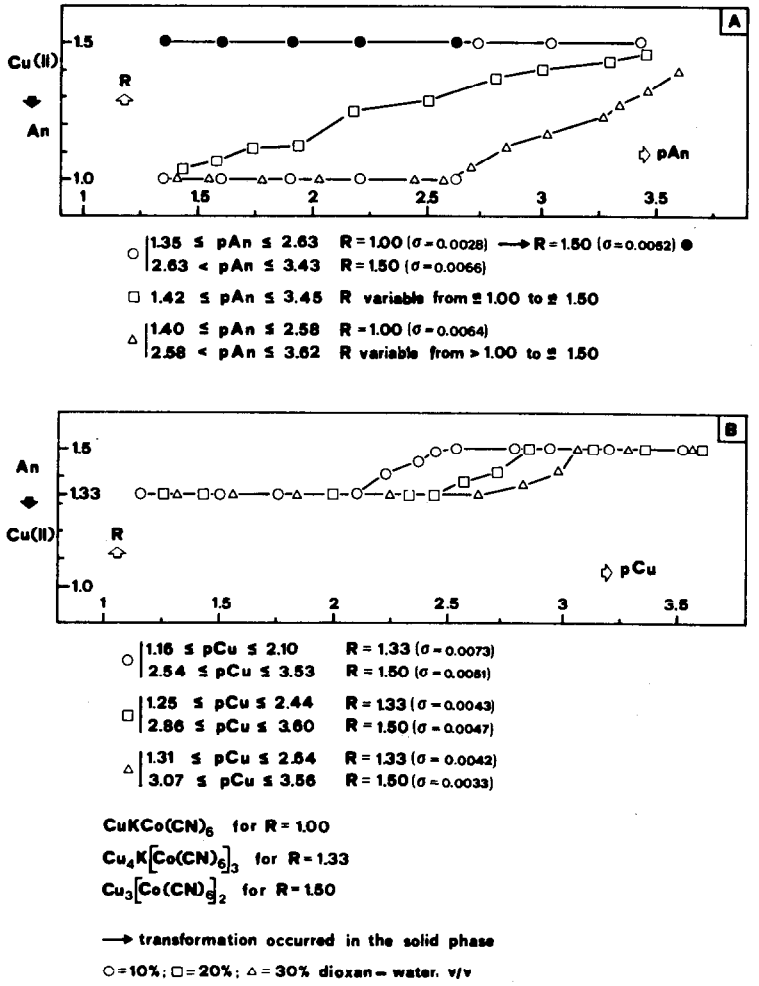

Fig. 1. Cu(II)–water–dioxan system. *R* values and relative standard deviations as obtained for different Cu(II) and An concentrations at varying dielectric constant of solvent medium. (A) An titrated with Cu(II); (B) Cu(II) titrated with An.

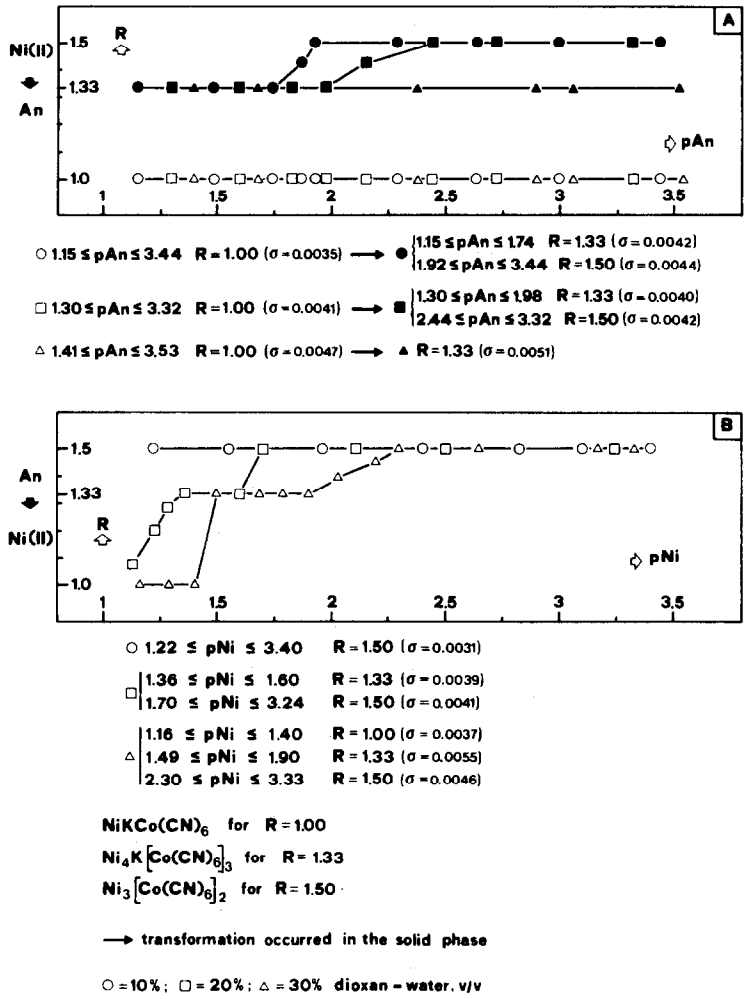

Fig. 2. Ni(II)–water–dioxan system. R values and relative standard deviations as obtained for different Ni(II) and An concentrations at varying dielectric constant of solvent medium. (A) An titrated with Ni(II); (B) Ni(II) titrated with An.

medium,[10] the influence of the K^+–$Co(CN)_6^{3-}$ species on the precipitation stoichiometry should become more marked as the dielectric constant of the solvent medium shifts from 80 (for water) to lower values (for mixtures of water with organic solvents of low dielectric constant). We have therefore decided to examine this experimentally as an extension of the earlier work.

EXPERIMENTAL

The dielectric constant of the solvent medium (ϵ) was varied by using 10, 20 and 30% v/v dioxan solutions in water.

Stock solutions of copper, nickel and zinc sulphates were prepared and standardized; the working solutions containing the desired amounts of dioxan were prepared by dilution. The hexacyanocobaltate solutions were similarly prepared and periodically standardized.

The equivalence point of the precipitation reactions (performed at 20 ± 1°) was detected with an oscillometric digital read-out apparatus.[11] For each titration the ratio (R) of the analytical metal ion and hexacyanocobaltate concentrations at the equivalence point was calculated.

The concentration range examined was the widest consonant with reagent solubility and the instrumental sensitivity. No buffer solutions were added and therefore the titration pH was that engendered by the solutions used in the reaction. The initial volume of solution titrated was always 100 ml and the reactant concentrations were chosen accordingly. All precipitates with a defined composition were analysed for cation and cobalt content by atomic-absorption spectrophotometry. For titration results leading to the same compound, the standard deviation, σ, was calculated.

Reactions between Cu(II) and $K_3Co(CN)_6$ (Fig. 1)

The compounds found were all intensely blue, with $R = 1.00$ corresponding to $CuKCo(CN)_6$, $R = 1.50$ corresponding to $Cu_3[Co(CN)_6]_2$ and $R = 1.33$ corresponding to $Cu_4K[Co(CN)_6]_3$ and stoichiometrically equivalent to $CuKCo(CN)_6 + Cu_3[Co(CN)_6]_2$, besides intermediate values in passing from one species to another.

When the Cu(II) is used as titrant for $1.35 \leqslant pAn \leqslant 2.63$ in 10% dioxan solution (An = anion), the compound first formed has $R = 1.00$, and is transformed in the solid phase, by addition of Cu(II), into the compound with $R = 1.50$.

When Cu(II) is the titrand, the species having $R = 1.33$ is preferentially formed, the range of conditions for its formation increasing as ϵ decreases.

In aqueous medium, the species with $R = 1.50$ was always obtained.

Reactions between Zn(II) and $K_3Co(CN)_6$

The only species found were those with $R = 1.00$ and $R = 1.50$, just as in aqueous medium. Decrease in ϵ, how-

ever, increased the tendency to formation of $ZnKCo(CN)_6$. In fact, with Zn(II) as the titrant, the compound with $R = 1.00$ was always precipitated irrespective of the conditions, and then underwent transformation in the solid phase to $Zn_3[Co(CN)_6]_2$. In contrast, in aqueous medium this transformation was limited to a restricted concentration range, only the species with $R = 1.50$ being normally obtained.

With Zn(II) as titrand the species with $R = 1.00$ was stabilized at the lowest ϵ value. This species was not obtained in purely aqueous medium. The precipitates were white.

Reactions between Ni(II) and $K_3Co(CN)_6$ (Fig. 2)

Precipitates with $R = 1.00$, $R = 1.33$ and $R = 1.50$ were found, as in aqueous medium, but decrease in ϵ stabilized the first two compounds over a wider range of conditions. Thus with Ni(II) as titrand in aqueous medium, the $Ni_3[Co(CN)_6]_2$ species was exclusively obtained, but in 30% dioxan medium, at high Ni(II) concentrations the $NiKCo(CN)_6$ species was stabilized. An analogous trend occurred with Ni(II) as titrant. The precipitates were blue.

DISCUSSION

The results show that the dielectric constant of the medium influences the stoichiometry by favouring the presence of potassium in the precipitates. Decrease in ϵ causes an increase of the K^+–$Co(CN)_6^{3-}$ ion-pair formation constant, so that for a fixed $K_3Co(CN)_6$ analytical concentration, the effective ion-pair concentration is the higher the smaller the ϵ value. Consequently, the reactions with K^+–$Co(CN)_6^{2-}$ are favoured rather than those with $Co(CN)_6^{3-}$.

Also the structure of the precipitates plays a positive role in formation of the mixed hexacyanocobaltates, as can be verified through localization of the metal ion and bonds in the crystal lattice.

In fact, two types of environment for the metal ion can be distinguished,[12] denoted by Me_I and Me_{II}. The former is present in the spatial group (4 Co, 4 Me_I, 2 Me_{II}, 24 C, 24 N) in 1:1 ratio with $Co(CN)_6^{3-}$ and bound in an Me_I–N–C–Co chain; the other two Me_{II} ions are statistically distributed and very weakly co-ordinated. Therefore, for the empirical formula, the configuration Me_I $Me_{II\,1/2}Co(CN)_6$ occurs. Consequently, the ions in the Me_{II} positions, because of these characteristics, are mobile and can be partially or totally substituted by potassium, to give the $MeKCo(CN)_6$ and $Me_4K[Co(CN)_6]_3$ species; this can occur both during the precipitation as well as later in the solid phase, and is favoured by the pre-existence of K^+–$Co(CN)_6^{3-}$ ion-pairs.

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RAPID DETERMINATION OF MILLIGRAM AMOUNTS OF URANIUM IN ORGANIC COMPLEXES WITH PYRIDINE-2,6-DICARBOXYLIC ACID AS TITRANT AND ARSENAZO I AS INDICATOR AFTER OXYGEN-FLASK COMBUSTION

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Summary—A method is described which allows the determination of uranium in organic complexes, following decomposition by the oxygen-flask procedure. Uranium is quantitatively determined by a direct titration with 0.01*M* pyridine-2,6-dicarboxylic acid, arsenazo I being used as the indicator. The end-point is sharp and the equilibrium is rapidly attained, so the titration can be carried out rapidly. The method is simple, rapid and highly reproducible.

Our long-range interest in the synthesis and characterization of new uranium complexes prompted us to develop a rapid and useful method for the determination of uranium. As in most elemental analyses, the problem is twofold, *i.e.*, decomposition of the organic material and determination of uranium after its dissolution. The reported ignition[1] and wet decomposition[2] procedures are of limited precision when small quantities of uranium are involved and are time-consuming. However a rapid method of oxygen-flask decomposition has been recently reported.[3,4]

For the subsequent determination of the uranium, gravimetric,[5-7] titrimetric[8-12] and spectrophotometric[13-18] methods have been proposed. The titrimetric methods are usually preferred when high precision and rapidity are required.

Titrimetric methods reported for the uranium determination are based on oxidation,[8,9] reduction,[10,11] and indirect titrations.[3,12] Owing to the preliminary reduction of uranium(VI) to uranium(IV), the oxidimetric method involves one step more than a direct reductimetric titration, and this step requires close control. On the other hand, direct reductimetric titrations suffer from the need for strong reductants that are unstable.

Indirect methods are based on the precipitation of uranium(VI) followed by back-titration of excess of the precipitant. The filtration makes the process time-consuming and inexact.

In this paper, we describe a decomposition of uranium complexes by oxygen-flask combustion followed by a titrimetric determination of uranium(VI) with a new titrant, pyridine-2,6-dicarboxylic acid (H_2PDC), that forms a soluble and very stable complex with uranium(VI).

EXPERIMENTAL

Reagents

The complexes bis(ethylcarbamato)dinitratodioxouranium(VI), pyridine N-oxide-bis(tropolonato)dioxouranium(VI), bis(dimethylsulphoxide-2,6-pyridinedicarboxylato-dioxouranium(VI), *cis*-dichloro-[*meso*-bis(*trans*-2-hydroxycyclohexyl)sulphide-OOS], dioxouranium(VI) and dioxobis(tropolonato)uranium(VI) were prepared as reported earlier.[19-23]

* Schleicher and Schüll No. 582[2] or equivalent.

Benzoyl peroxide. Recrystallized by dissolving it in chloroform at room temperature and adding twice the volume of methyl alcohol. Stored in a dark bottle.

pH indicator. Bromophenol Blue, 0.5% alcoholic solution.

Buffer solution. Acetate–acetic acid, 0.2*M*, pH 3.6.

Titration indicator. Arsenazo I [2-(*o*-Arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid, trisodium salt], 0.1% aqueous solution.

*Pyridine-2,6-dicarboxylic acid solution, 0.01*M. Pyridine-2,6-dicarboxylic acid (1.67 g) dissolved in 150 ml of ethanol and diluted to 1000 ml with distilled water. Standardized against 0.02*M* sodium hydroxide.

Uranyl nitrate solution. Uranyl nitrate (1.20 g) dissolved in water and diluted to 1000 ml.

All reagents were of microanalytical reagent grade.

Procedure

Transfer a suitable weighed amount of sample (4–15 mg) and approximately 10 mg of powdered benzoyl peroxide to an L-shaped ash-free filter paper* (2.7 × 3 cm). Wrap the sample and benzoyl peroxide in the paper, and clamp the resulting packet firmly in the platinum gauze holder of a 300-ml oxygen-combustion flask. Use 5 ml of 5*M* nitric acid as absorbant medium. Fill the flask with pure oxygen and carry out the combustion. When the combustion is complete, shake the solution for 4–5 min, until the white fumes disappear. Remove the stopper, rinse the walls of the flask and the platinum gauze with 5 ml of distilled water. Evaporate nearly to dryness, then add 5 ml of distilled water and finally evaporate again nearly to dryness. Dissolve the residue in 40 ml of distilled water and add 1 drop of Bromophenol Blue indicator solution. Add 1*M* sodium hydroxide to bring the pH to 3–4 (colour grey–green). Add 3 ml of buffer solution (pH 3.6), 0.3 ml of arsenazo I solution and titrate with 0.01*M* H_2PDC. The end-point is sharp, from blue to bright pink.

1 ml of 0.01*M* $H_2PDC \equiv 2.381$ mg of uranium

RESULTS AND DISCUSSION

H_2PDC is a multidentate ligand able to form monomeric or polymeric species by co-ordination with uranyl and other metal ions in aqueous solution, depending on the experimental conditions.[19-33] The use of H_2PDC in presence of tetraphenylarsonium chloride for gravimetric determination of uranium has been reported in a previous paper.[34] In view of the solubility and high stability of

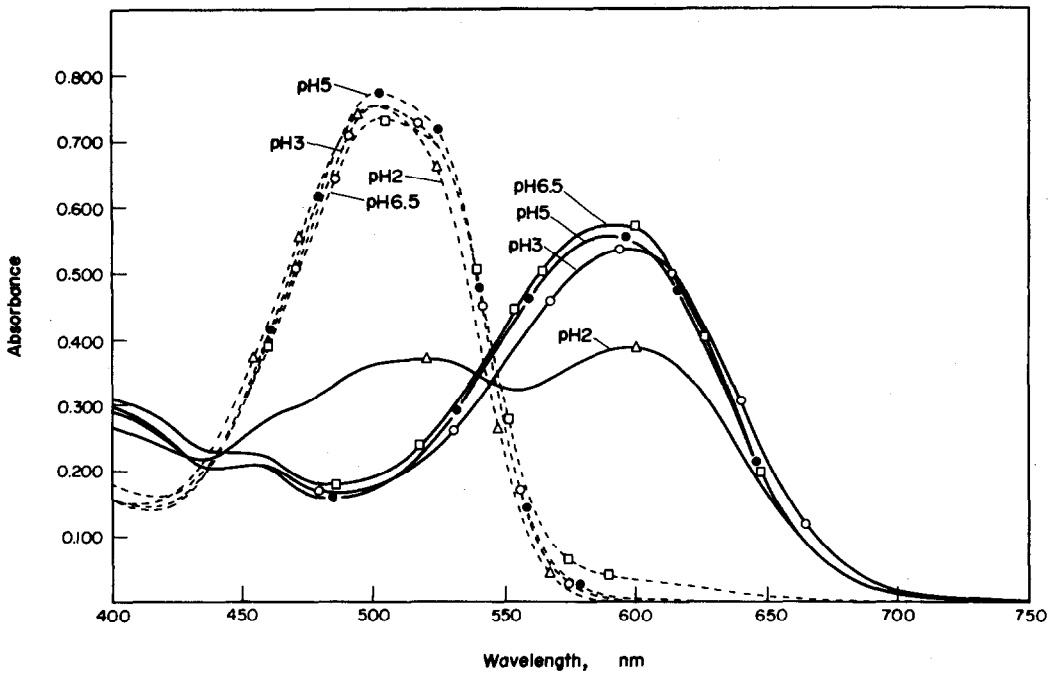

Fig. 1. Absorption spectra of aqueous solution of uranium–arsenazo I complex at different pH values. Uranyl nitrate standard solution (5 ml) and 0.5 ml of 0.1% aqueous arsenazo I solution diluted to 25 ml with distilled water; 1-cm cells —— 0.3 ml before end-point; – – – 0.3 ml after end-point.

the complex of uranyl ions with H_2PDC, we decided to investigate the possibility of using this ligand as a titrant for uranium. Arsenazo I is used as a direct titrimetric indicator. Arsenazo II and arsenazo III can also be used, but the best results have been obtained with arsenazo I.

The absorption spectra of the uranyl nitrate solution just before and after the end-point are completely different, the wavelength of maximum absorption having shifted from 600 to 510 nm, corresponding to the release of arsenazo I from its uranium complex. The effect of pH on the titration has been studied over a pH range of 2.0–6.5 (Fig. 1). The absorption spectra show that the uranium–arsenazo I complex is formed at pH 3–6[14] and suggest that the uranium–H_2PDC complex is formed at pH 2–6.

This method appears to offer a very promising procedure for the determination of uranium in organic complexes, with a simple titrimetric finish. Accordingly the procedure has been closely examined to establish the optimum conditions.

For the combustion of the sample, we chose the oxygen-flask method which is a rapid routine procedure. Benzoyl peroxide is added to ensure complete combustion.[35] Nitric acid (5*M*) acts as an efficient absorbent and also ensures complete dissolution of all the oxides formed. As the nitric acid must be neutralized and an excess of salts makes the end-point less sharp, the absorption solution is evaporated nearly to dryness.

The titration of UO_2^{2+} with 0.01*M* H_2PDC was carried out with different amounts of the indicator solution and

Table 1. Results obtained in the determination of uranium with H_2PDC as titrant

Compounds	Weight range taken. *mg*	Uranium, % Theoretical	Uranium, % Found	Std. devn., %
Bis(ethylcarbamate)-dinitratodioxouranium(VI) $C_6H_{14}N_4O_{12}U$	3.7–20.8	41.60	41.0–42.2	0.27 (31 results)
Pyridine oxide–bis-(tropolonato)dioxouranium(VI) $C_{19}H_{15}NO_7U$	7.2–13.5	39.20	39.1–39.4	0.14 (6 results)
Bis(dimethylsulphoxide)-2,6-pyridinedicarboxylato-dioxouranium(VI) $C_{11}H_{15}NO_8S_2U$	4.6–9.2	40.25	40.1–40.5	0.16 (6 results)
Cis-dichloro[meso-bis(*trans*-2-hydroxycyclohexyl)sulphide-OOS]dioxouranium(VI) $C_{12}H_{22}Cl_2O_4SU$	6.3–11.6	41.67	41.4–41.9	0.17 (6 results)
Dioxobis(tropolonato)-uranium(VI) $C_{14}H_{10}O_6U$	6.5–18.0	46.47	46.3–46.6	0.12 (6 results)

at different pH values. The most distinct colour change at the end-point is obtained at pH 3.6, with 0.3 ml of 0.1% aqueous arsenazo I solution. The H_2PDC forms, under the suggested conditions, a 1:1 complex with uranyl ions. The equilibrium at the end-point is rapidly attained, so the titration can be performed quickly.

Typical results for standard samples and for several recently synthesized uranium complexes are listed in Table 1. The absolute error is $\pm 0.6\%$, the mean error and standard deviation being $+0.1\%$ and 0.3% respectively. Hence the method is quite reliable and it is both rapid and simple.

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ANION-EXCHANGE STUDIES OF METAL THIOCYANATES IN AQUEOUS AND MIXED SOLVENT SYSTEMS

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Summary—The anion-exchange behaviour of metal ions in aqueous NH_4CNS and aqueous NH_4CNS-organic solvent mixtures has been studied. The effect of the pH and the concentrations of thiocyanate and organic solvent on the distribution coefficients has been investigated. Fifteen binary metal ion separations are reported.

The ion-exchange behaviour of metals in aqueous thiocyanate solution has been a subject of considerable interest. Surls and Choppin[1] studied the behaviour of lanthanides and actinides on strongly anionic and cationic resins in aqueous ammonium thiocyanate solution. Turner *et al.*[2] investigated the behaviour of scandium and some transition elements on Dowex 1 in aqueous potassium thiocyanate solution and carried out a few separations. Some of the metals could not be eluted because of their strong adsorption on the resin. Hamaguchi and co-workers[3,4] achieved a few anion-exchange separations in ammonium thiocyanate–hydrochloric acid media. Majumdar and Mitra[5] carried out some separations from aqueous thiocyanate solution: a few strongly adsorbed metal ions were not eluted from the column. Metal ions have also been separated as thiocyanates on weakly basic resins[6] and cellulose ion-exchangers.[7–9]

In the last two decades Korkisch and co-workers[10–15] have advanced the technique of combined ion-exchange and solvent extraction (CIESE) and demonstrated its potential by carrying out several difficult separations from various aqueous organic media.

The present communication reports an investigation of CIESE applied to thiocyanates, and the variation in the distribution coefficients of thirteen metal ions on Dowex 1 with ammonium thiocyanate concentration and percentage of organic solvent.

EXPERIMENTAL

Dowex 1–X8 (20–50 mesh) was converted into the thiocyanate form by equilibration with 1.0*M* ammonium thiocyanate. A metal sulphate solution ($1.0 \times 10^{-4}M$) labelled with the appropriate radioisotope was used for the determination of distribution coefficients by the batch method. For silver and yttrium, nitrate solutions were used. The radioisotopes used were procured from Bhabha Atomic Research Centre, Bombay, India. The gamma activity of ^{51}Cr, ^{54}Mn, ^{58}Co, $^{55+59}Fe$, ^{65}Zn, ^{110m}Ag, ^{114m}In, ^{160}Tb and ^{203}Hg was counted on an NaI(Tl) well-type scintillation counter. Beta-counting of ^{91}Y, ^{115m}Cd and ^{204}Tl was done with a Geiger counter. For column separations a glass column (3 cm long, 1 cm bore) was employed. A flow-rate of 10 ml/hr was maintained throughout the separation procedure.

RESULTS AND DISCUSSION

Effect of pH on distribution coefficients

The effect of pH on the K_d values was studied in 1.0*M* ammonium thiocyanate. Within the pH range 3.0–5.0 the distribution coefficients do not change. The pH of the $1.0 \times 10^{-4}M$ metal ion solutions in 0.1–4.0*M* ammonium thiocyanate lies within the range 3.0–5.0, so any change in K_d values with change in hydrogen-ion concentration is insignificant.

Effect of ammonium thiocyanate concentration

The dependence of the distribution coefficients on the

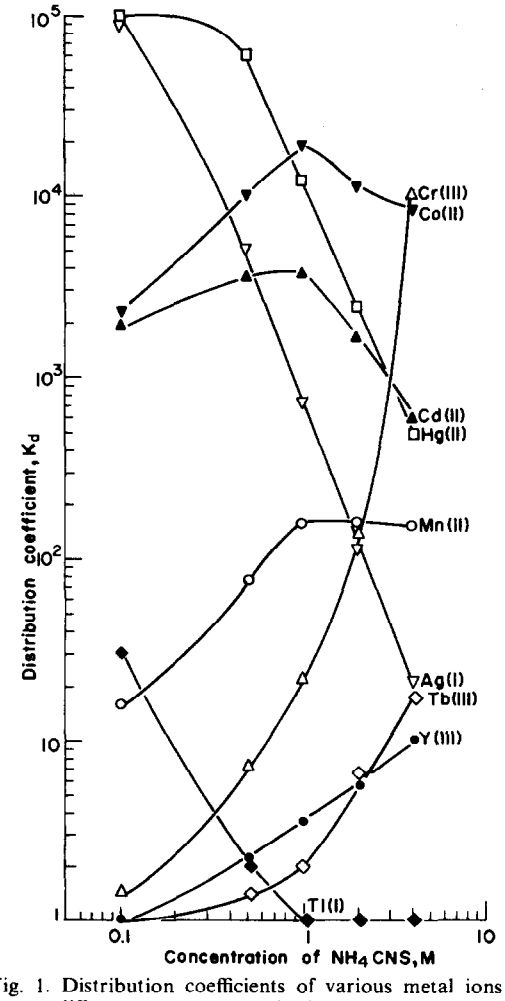

Fig. 1. Distribution coefficients of various metal ions at different aqueous NH_4CNS concentrations.

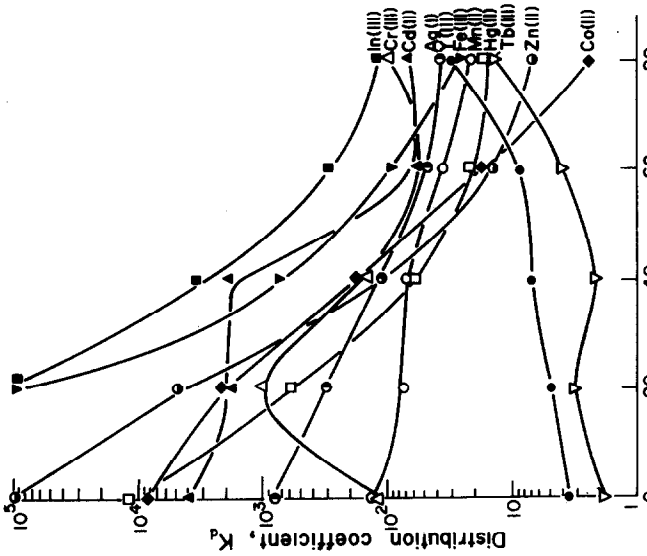

Fig. 4. Variation of distribution coefficients of different metal ions with percentage of THF (tetrahydrofuran) at constant overall 1.0*M* NH_4CNS concentration.

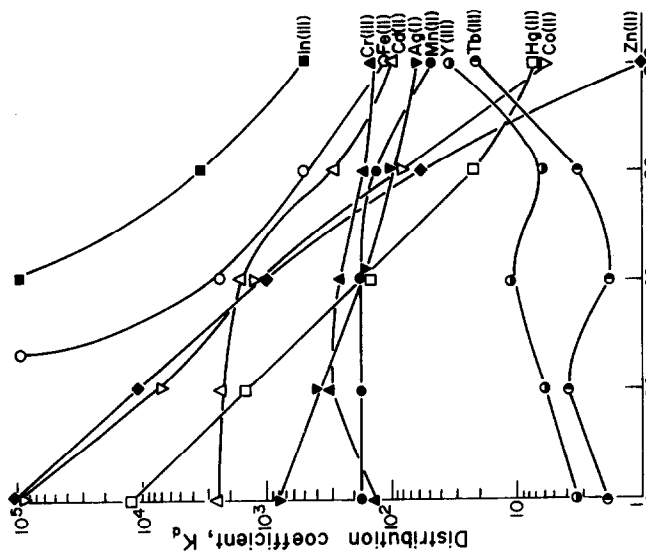

Fig. 3. Variation of distribution coefficients of different metal ions with percentage of acetone at constant overall 1.0*M* NH_4CNS concentration.

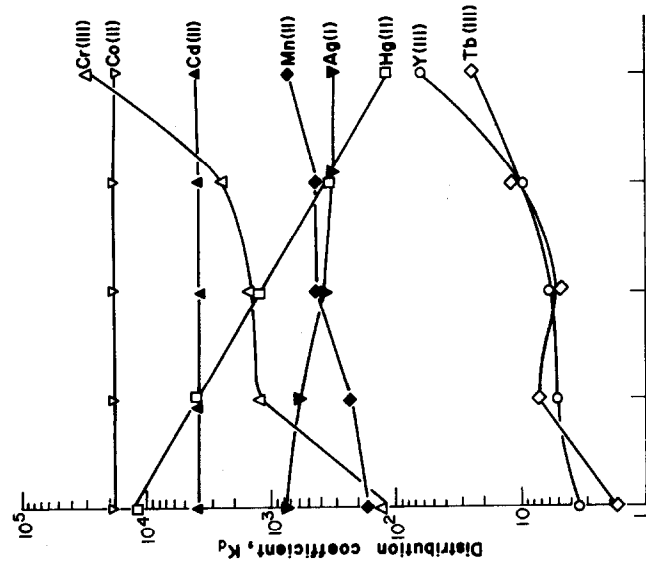

Fig. 2. Variation of distribution coefficients of different metal ions with percentage of methanol at constant overall 1.0*M* NH_4CNS concentration.

Table 1. Details for the separation of metal ions on Dowex 1-X8 (20–50 mesh)

Separation*	Eluent, *ml*†	Loading, *μg*	Recovery, *μg*
Zn(II)[a]–Fe(III)[b]	a 20; b 20	13.0; 11.0	12.2; 11.0
Tl(III)[c]–Zn(II)[a]	c 24; a 30	41.0; 13.0	41.0; 11.7
Tl(III)[c]–Cd(II)[d]	c 24; d 26	41.0; 25.0	41.0; 25.0
Tl(III)[c]–Hg(II)[a]	c 24; a 30	41.0; 40.0	41.0; 39.3
Tl(III)[c]–In(III)[d]	c 24; d 26	41.0; 23.0	41.0; 21.6
Cr(III)[c]–Co(II)[a]	c 20; a 20	10.4; 13.8	10.4; 13.8
Cr(III)[c]–Fe(III)[b]	c 20; b 20	10.4; 11.0	10.4; 11.0
Mn(II)[c]–Zn(II)[a]	c 20; a 20	11.0; 13.0	10.4; 11.7
Mn(II)[c]–Co(II)[a]	c 20; a 20	11.0; 10.4	10.4; 10.4
Mn(II)[c]–Fe(III)[b]	c 20; b 20	11.0; 13.0	10.4; 11.7
Co(II)[a]–Fe(III)[b]	a 20; b 20	11.0; 11.0	10.4; 11.0
Ag(I)[e]–Zn(II)[a]	e 42; a 30	21.5; 13.0	21.5; 11.7
Ag(I)[e]–Hg(II)[a]	e 42; a 30	21.5; 40.0	21.4; 39.3
Y(III)[c]–In(III)[d]	c 16; d 26	17.8; 23.0	16.9; 21.8
Tb(III)[c]–In(III)[d]	c 16; d 26	31.8; 23.0	31.1; 21.8

* Separations were carried out in the order given, superscripts denoting the eluents used.

† a 1.0*M* NH_4CNS–80% acetone, b 1.0*M* HCl–80% acetone, c 0.1*M* NH_4CNS, d 0.05*M* EDTA, e 7.0*M* NH_4CNS.

ammonium thiocyanate concentration is shown in Fig. 1. For K_d values less than 1 and greater than 10^5 the points are recorded as 1 and 10^5 respectively. The sorption of Zn, Fe(III) and In(III) is almost complete ($K_d \geqslant 10^5$) and that of Tl (III) is practically negligible ($K_d \leqslant 1$) over the entire range. The sorption of Cr(III), Y(III) and Tb(III) increases with increasing thiocyanate concentration and that of Ag(I), Tl(I) and Hg(II) shows the opposite trend. A maximum at around 1*M* ammonium thiocyanate is observed in the case of Co(II) and Cd(II). The sorption of Mn(II) increases up to 1*M* thiocyanate and thereafter becomes almost constant.

Effect of organic solvent concentration

The solvent effect is shown in Figs. 2–4. In acetone and tetrahydrofuran media the distribution coefficients of Ag(I), Co(II), Zn(II), Cd(II), Hg(II), Fe(III) and In(III) decrease with increasing organic solvent content while those of Y(III) and Tb(III) increase. The sorption of Mn(II) does not change. In the case of Cr(III) a maximum is observed at around 20% tetrahydrofuran but its sorption is unaffected by increasing acetone content. Methanol has little effect on the distribution coefficients. A similar observation was made by Korkisch and Ahluwalia[12] who attributed it to the weak Lewis base character of methanol compared to acetone and tetrahydrofuran.

Metal separations

Fifteen representative separations have been achieved and are listed in Table 1. Strongly sorbed metal ions such as Co(II), Zn(II) and Hg(II) are conveniently eluted with 1.0*M* ammonium thiocyanate–80% acetone mixture. For Cd(II) and In(III) 1.0*M* ammonium thiocyanate–80% tetrahydrofuran can be used for desorption but the recovery is only 75%. Therefore in an actual separation procedure 0.05*M* EDTA is used as the eluent for quantitative recovery. The desorption of Fe(III) presented a problem and was carried out with 1.0*M* hydrochloric acid–80% acetone.

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THE SOLVENT EXTRACTION OF IRON FROM STEEL SOLUTIONS WITH 2-HEXYLPYRIDINE PRIOR TO THE DETERMINATION OF TRACE ELEMENTS

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Summary—The distribution of iron(III) between aqueous hydrochloric acid and 0.1*M* 2-hexylpyridine in benzene was examined as a function of acid concentration in the aqueous solution, the metal concentration being kept constant, and as a function of increasing ferric chloride concentration at a constant acidity of hydrochloric acid. The distribution coefficient of Fe(III) (tracer) is dependent on the square of the 2-hexylpyridine concentration in the benzene phase. Negatively charged complexes of the type $FeCl_5^{2-}$ may be the species extracted. The formation of a mixture of 1:1 and 1:2 complexes with 2-hexylpyridine is indicated. Salting-out effects of a number of salts have been investigated. Separation factors of several metal ions relative to iron(III) in 7*M* hydrochloric acid are also reported. The results indicate that iron(III) can be selectively separated from a large number of elements, and the method has been utilized for the preconcentration of non-ferrous metal ions in mild steels by selective separation of iron, before their subsequent determination by emission spectrometry.

The effectiveness of a chemical technique of separation and concentration is principally dependent on its selectivity. In our investigations of long-chain alkyl-substituted pyridines in solvent extraction, we have found that 2-hexylpyridine is useful in the selective separation of some metal ions which form anionic complexes in aqueous solution, *e.g.*, gold(III)[1] and chromium(VI).[2] This report extends the work to iron(III) in hydrochloric acid media and shows that it can be selectively separated from a large number of metal ions. The results can be utilized to remove iron before determination of the trace elements in steels by various instrumental methods.

EXPERIMENTAL

Solutions

2-Hexylpyridine was dissolved in benzene to give a 0.1*M* solution. Stock solutions of the test elements were prepared. The other reagents used were the same as reported previously.[3]

Sample preparation

A 900-mg sample of SS—456 mild steel (British Chemical Standards) was dissolved in 7*M* hydrochloric acid and the solution made up to 50 ml with the same acid.

Tracers and equipment

The following isotopes were used: ^{59}Fe, ^{60}Co, ^{64}Cu, ^{198}Au, ^{65}Zn, ^{99}Mo, ^{99m}Tc, ^{144}Ce, ^{106}Ru, ^{203}Hg and ^{233}U. Carrier-free iron-59 was obtained as previously reported.[4] The other tracers used were obtained from the Radiochemical Centre, Amersham or prepared locally by (n,γ) reactions or by separation of the daughter nuclide from the parent without a carrier. The equipment used for the radiochemical assay is described elsewhere.[1,5]

Partition equilibria

Extraction experiments were performed with 1 ml of each phase at 23 ± 3°. Equilibrium was attained in *ca.* 3 min so 5-min extractions were carried out. After the phases had separated the γ-activity was measured on 500 μl of each phase with an NaI(Tl) crystal and a Nuclear Chicago Single Channel Analyser, Model 872. In some cases the degree of extraction was determined from α- or β-activity; in such instances the aliquots of both phases were transferred to glass planchettes and evaporated under an infrared lamp, and the radioactivity was then measured. The distribution ratio and percentage extraction were calculated in the usual manner. The extraction of other metal ions was studied in 7*M* hydrochloric acid medium containing 18 mg of Fe(III) per ml.

Analytical procedure

One ml of the standard or the sample solution containing indium as the internal standard (100 μl of 500-ppm indium solution in 1 ml) was equilibrated with two 1-ml portions of 0.25*M* 2-hexylpyridine in benzene for 5 min. The aqueous phase was evaporated to about 0.5 ml and then evaporated in a graphite electrode coated with Apiezon M and containing 10 mg of graphite and 5 mg of Teflon powder. The content of test elements in the extraction standards varied between 10^{-2} and 10^{-5}%. A 3.4-m Ebert-type Jarrell-Ash spectrograph in conjunction with d.c. arc excitation was used for the analysis.

RESULTS AND DISCUSSION

The extraction of iron(III) ($< 10^{-6}$ *M*) from hydrochloric acid by 0.1*M* 2-hexylpyridine in benzene gave the results shown in Fig. 1. It is seen that the extraction begins at moderate acidity and increases with increasing acid concentration. This is perhaps due to extraction of undissociated complex metal acid species of the type H_nFeCl_{3+n} (where $n = 1,2$). Figure 1 also shows the extraction data for use of 0.1*M* 5-(4-pyridyl) nonane (PyN) and tri-n-octylamine (TOA) dissolved in benzene; it appears that alkyl-substituted pyridines are poorer extractants than tri-n-octylamine for iron. This is because TOA, being a stronger base than HPy and PyN, forms salts in less acidic media, which explains the shift of the extraction curve to this region relative to the same curves for PyN and HPy. Despite its lower extraction power, PyN is the most selective reagent for isolating iron(III) because the extraction of a

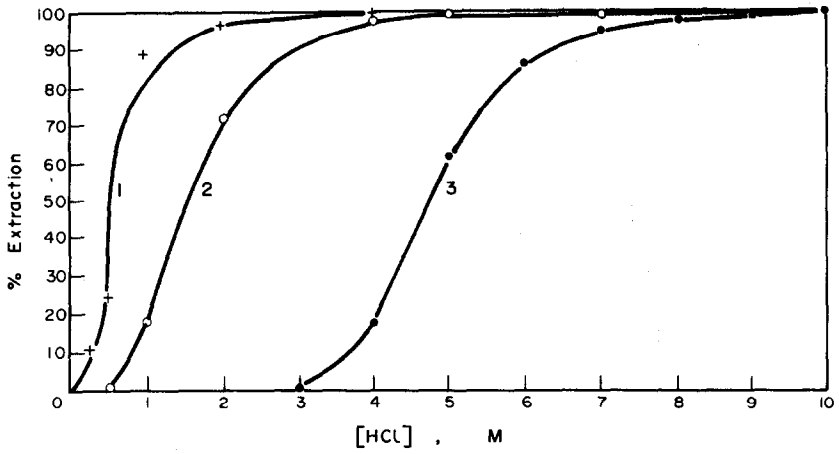

Fig. 1. The degree of extraction of iron(III) into 0.1*M* tri-n-octylamine, 5-(4-pyridyl) nonane and 2-hexylpyridine in benzene as a function of hydrochloric acid concentration in the aqueous phases. 1—TOA; 2—PyN; 3—HPy.

number of metal ions (except some of those which form complex metal acids in aqueous solution) is very poor.

The effect of inert electrolytes on the extraction of iron(III) at constant acidity (0.1, 0.5, 1.0*M* acid) was examined. The concentration of the chlorides of Li^+, Na^+, K^+, Mg^{2+} and Al^{3+} was varied between 0.01 and 5*M*. The degree of extraction increased with increasing chloride concentration, as would be expected, and was also enhanced by the cations with the highest hydration energy; thus the order of efficiency as salting-out agents was $AlCl_3$ > $MgCl_2$ > NaCl > LiCl > KCl. Extraction with potassium chloride added was poor, and this was attributed to the lower electrical potential (*Ze/r*) of the potassium ion.

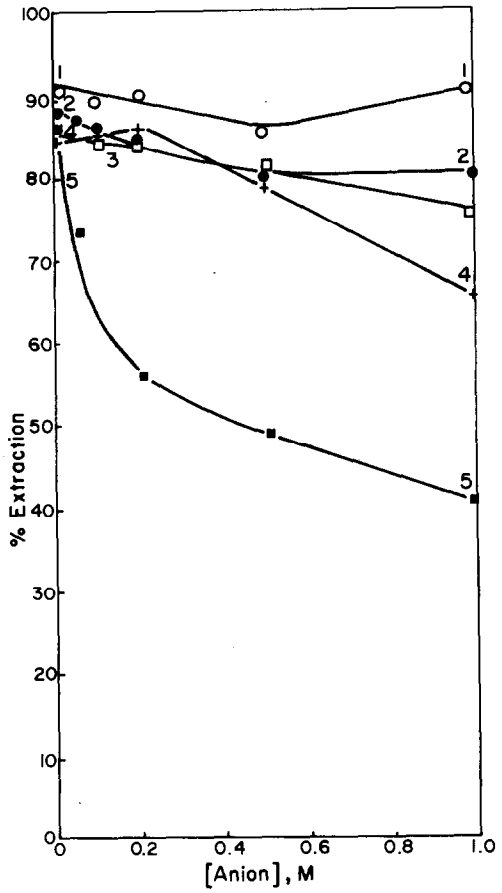

Fig. 2. Effect of various anions on the extraction of iron(III) from 7*M* HCl by 0.1*M* 2-hexylpyridine in benzene. 1—nitrate; 2—citrate; 3—acetate; 4—oxalate; 5—ascorbate.

The plot of log *D* *vs.* log [PyN] at constant acidity (7*M* hydrochloric acid) was linear with a slope of 2. This could be explained by the extraction of $FeCl_4^-$ through mixed quadrupole formation as described for the PyN system[3] or through interaction with singly charged dimeric hexylpyridine hydrochloride ions, since the hydrochloride of this pyridine forms aggregated species if the hydrochloric acid concentration is above 1*M*. The results also agree, however, with the hypothesis of extraction of $FeCl_5^{2-}$ ions through ion-pair formation with pyridinium ions or as the undissociated complex acid, H_2FeCl_5, salted-out by the high acid concentration. The pyridine may also solvate the ion-pair as a whole, with or without hydration. The extraction through ion-associated complexes appears unlikely, as in general the extraction of anionic metal complexes by this pyridine is poor.

Loading experiments were also performed with 0.1–1*M* ferric(III) chloride in 7*M* hydrochloric acid. The plot of the ratio [Fe(III)]/[HPy] reached a maximum at 0.38 mg/ml, indicating the presence of a mixture of compounds containing one and two molecules of the extractant. The complex extracted could be a mixture of $HFeCl_4$ and H_2FeCl_5. The slope of the isotherm decreases with increasing concentration of iron in the aqueous phase. It is reasonable to assume that at high iron concentration the equilibrium shifts in favour of formation of H_2FeCl_5.

The effect of a number of anions on the extraction of iron from 7*M* hydrochloric acid was investigated. The results shown in Fig. 2 indicate that citrate, oxalate and acetate in concentrations up to 1*M* have little effect on the extraction of iron(III). Ascorbic acid decreases the degree of extraction, presumably because of reduction of iron(III) to iron(II).

The partition coefficients of several other elements between 7*M* hydrochloric acid and 0.1*M* solution of the pyridine were measured. The distribution coefficients and separation factors are reported in Table 1. It is to be noted that a number of elements, *e.g.*, uranium, niobium, zirconium, zinc, which form strong anionic complexes under these conditions, are not extracted by this amine. This behaviour is unlike that of all the commonly used solvating reagents and liquid anion-exchangers. This is probably because the amine does not form stable cations of the type $(HPyH)^+$ which could associate with the anionic metal

Table 1. Distribution coefficients and separation factor [with respect to iron(III)] of different metal ions in the 0.1*M* HPy/benzene–7*M* HCl system

Metal ion	Concentration, *M*	Distribution coefficient	Separation factor
Tc(VII)	*C.F.	0.030	$> 10^3$
Mn(VII)	10^{-2}	0.0009	2.1×10^4
Mo(VI)	10^{-5}	0.025	$> 10^3$
U(VI)	10^{-3}	0.0015	1.2×10^4
Cr(VI)	C.F.	0.0004	4.7×10^4
V(V)	10^{-3}	$< 10^{-3}$	$> 10^4$
Nb(V)	C.F.	$< 10^{-2}$	$> 10^3$
Mo(V)	10^{-5}	0.0130	1.4×10^3
Sb(V)	10^{-6}	$< 10^{-3}$	$> 10^4$
Zr(IV)	10^{-8}	$< 10^{-2}$	$> 10^3$
Ru(IV)	10^{-8}	0.0031	6.1×10^3
Al(III)	10^{-5}	$< 10^{-3}$	$> 10^4$
Cr(III)	C.F.	$< 10^{-3}$	$> 10^4$
Ce(III)	10^{-8}	$< 10^{-3}$	$> 10^4$
Y(III)	10^{-8}	0.0008	2.3×10^4
Au(III)	10^{-6}	4.10	4.634
Sb(III)	10^{-6}	$< 10^{-3}$	10^4
Zn^{2+}	10^{-5}	0.0055	3.4×10^3
Hg^{2+}	10^{-7}	0.0091	2.0×10^3
Pb^{2+}	10^{-6}	$< 10^{-3}$	$> 10^4$
Sr^{2+}	10^{-8}	$< 10^{-3}$	$> 10^4$
Cu^{2+} (II)	10^{-6}	$< 10^{-2}$	$> 10^3$
Co^{2+}	10^{-7}	$< 10^{-3}$	$> 10^4$
Cs^+	10^{-8}	$< 10^{-3}$	$> 10^4$
Ag^+	10^{-8}	$< 10^{-3}$	$> 10^4$
Br^-	10^{-5}	0.0041	4.6×10^3

* C.F. = Carrier-free

complexes to give ion-pairs. Another plausible explanation is that the acid is extracted by participation of the hydrated proton (H_3O^+) because the pyridine is a weak base and the proton of the acid may add on, not to the nitrogen atom of the pyridine, but to the basic oxygen atom of the strongly polarized water molecule, resulting in the formation of a simple oxonium ion and combination of the complex with the hydrolysed HPy cation $(HPyH \cdot H_2O)^+$, making the species unstable and thus inextractable. Utilizing the high selectivity of iron(III) extraction, we determined the trace elements in mild steels by emission spectrography. The results are illustrated in Table 2.

Table 2. Analysis of mild steel (SS-456; British Chemical Standards) by the proposed method

Element	Amount certified, *ppm*	Amount found, *ppm**	Average error, %
Si	2200	2260, 2340, 2450	+ 7
Mn	1700	1730, 1780, 1860	+ 5
V	240	224, 232, 235	− 4
Co	480	390, 407, 432	− 15
Zr	340	312, 325, 352	− 3
Al	80	73, 93, 105	+ 13
Pb	100	77, 82, 116	− 8
Sb	110	72, 80, 104	− 11
Nb	50	31, 38, 52	− 20
B	10	9, 11, 14	+ 12

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ANALYTICAL DATA

AUTOPROTOLYSIS CONSTANTS AND ACID–BASE PROPERTIES OF PROPYLENE GLYCOL MIXTURES

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Summary—The autoprotolysis constants of propylene glycol and its mixtures with water, acetone, propan-2-ol and chloroform have been determined potentiometrically. In the same solvent mixtures the protolysis constants of the phthalic acid–hydrogen phthalate system have been evaluated and indicate that the solvent is more acidic than water, but less acidic than ethylene glycol.

Propylene glycol (propane-1,2-diol) and its mixtures have been used as solvents in acid–base titrations. Their properties are similar to those of ethylene glycol and its mixtures, but it has been claimed[1] that propylene glycol is advantageous because of the greater solubility in it of organic compounds, *e.g.*, soaps. The value of the autoprotolysis constant of propylene glycol has been reported previously and corresponds to $pK_s = 17.21$ at 25°,[2] but there are no data for mixtures of propylene glycol with water and organic solvents. These mixtures are important in practical determinations because of the lower viscosity and more rapid equilibration.

To obtain data for the acid–base properties of propylene glycol and its mixtures it was necessary to determine the dissociation constant of an acid or of a base used as a standard. Zikolov, Astrug and Budevsky[3] in their study of ethylene glycol used hydrogen phthalate as a standard and in order to compare the two solvents we have used the same substance. With pure propylene glycol as solvent the basic dissociation constant of hydrogen phthalate corresponds to $pK_b = 9.97$.[4]

EXPERIMENTAL

Reagents

Propylene glycol was purified by distillation under reduced pressure. The water content, checked coulometrically by the Karl Fischer method, was less than 0.05%.

Potassium chloride and potassium hydrogen phthalate (analytical grade) were further purified by crystallization.

Solutions of acid titrants were prepared by dilution of a saturated solution of hydrogen chloride in propylene glycol with the appropriate solvent. The titre of all solutions [C in cells (1) and (6)] was determined by potentiometric titration of hydrogen phthalate in the same solvent (SH).

Solutions of sodium propanediolate approx. 0.01M [C_1 in cell (1)] were prepared by the action of metallic sodium on the solvent.

Solutions containing the appropriate concentration of potassium chloride were added to keep the concentration of chloride ion constant (C) during titrations. The ionic strength I of the solutions was in the range 0.032–0.079.

Apparatus

A Radiometer PHM 64 pH meter with a G 202 B glass electrode (GE) was used in conjunction with a Metrohm E-415 autoburette and a temperature-controlled cell (25 ± 0.1°).

RESULTS

Determination of the autoprotolysis constant

For determination of the autoprotolysis constant the procedure described by Zikolov, Astrug and Budevsky[3] was applied. The emf of the cell

$$\text{GE} \parallel \text{Na propanediolate–}C_1, (\text{KCl} + \text{HCl})\text{–}C, \text{SH} \mid \text{AgCl–Ag} \quad (1)$$

was measured at 25°. For the acid and alkaline regions the following equations can be applied,

$$E = E_a^0 - 0.05916 \log [SH_2^+] \quad (2)$$

$$E = E_b^0 + 0.05916 \log [S^-] \quad (3)$$

where $[SH_2^+]$ and $[S^-]$ are the concentrations of lyonium and lyate ions respectively, and are calculated from the known concentrations, C_1 and C, of the components of the cell (1). E_a^0 and E_b^0 are constants characteristic of the cell in the acid and alkaline regions respectively. Thus

$$pK_s = (E_b^0 - E_a^0)/0.05916 \quad (4)$$

corresponds to a concentration autoprotolysis constant for a given ionic strength in the range 0.032–0.079. These values are recalculated to give the thermodynamic constant pK^T by use of the extended form of the Debye–Hückel equation,

$$-\log f = \frac{1.825 \times 10^6 (\epsilon T)^{-3/2} I^{1/2}}{1 + 251.45 (\epsilon T)^{-1/2} I^{1/2}} \quad (5)$$

Table 1. Autoprotolysis constants of propylene glycol and its mixtures at 25°C

Solvent	ϵ	I	pK_s^C	$-\log f$	pK_s^T
PrG	32.0	0.061	16.39	0.296	16.98
PrG + 1% W	32.5	0.040	15.93	0.253	16.44
PrG + 1.5% W	32.7	0.079	15.68	0.311	16.30
PrG + 3% W	33.4	0.079	15.33	0.302	15.93
PrG + 5% W	34.3	0.057	15.19	0.264	15.72
PrG + 12% W	37.6	0.054	14.64	0.231	15.10
PrG + 21% W	41.7	0.033	14.21	0.170	14.55
PrG + 20% Ch	26.5	0.050	16.82	0.356	17.53
PrG + 20% iPrOH	29.3	0.051	16.46	0.314	17.09
PrG + 20% A	29.7	0.058	16.22	0.321	16.86

* PrG–propylene glycol, W–water, Ch–chloroform, iPrOH–propan-2-ol, A–acetone.

Table 2. Protolysis constants of phthalic acid in propylene glycol and its mixtures at 25°C

Solvent*	ϵ	I	$pK^{C}_{H_2Ph}$	$-\log f$	$pK^{I}_{a(H_2Ph)}$	$pK^{I}_{b(HPh^-)}$
PrG	32.0	0.039	6.40	0.261	6.92	10.07
PrG + 1% W	32.5	0.041	5.87	0.255	6.38	10.07
PrG + 1.5% W	32.7	0.032	5.67	0.234	6.14	10.17
PrG + 3% W	33.4	0.020	5.55	0.189	5.93	10.00
PrG + 5% W	34.3	0.017	5.22	0.165	5.56	10.16
PrG + 12% W	37.6	0.032	4.57	0.196	4.96	10.14
PrG + 20% Ch	26.5	0.050	6.42	0.356	7.13	10.41
PrG + 20% iPrOH	29.3	0.051	6.19	0.315	6.82	10.27
PrG + 20% A	29.7	0.058	5.61	0.321	6.25	10.61

* Symbols as in Table 1.

In this equation the ion-size parameter was taken as 5 and the dielectric constant values (ϵ) used were as indicated in Table 1, assuming additivity for mixed solvents. All measurements were carried out at $T = 298$ K. The results presented in Table 1 for each mixture are mean values of 2 or 3 sets of measurements. The constancy of the E^0 values within one set was not worse than ± 0.4 mV, indicating the absence of systematic errors. The calculated values of pK_s from different sets do not differ by more than 0.03 units (except in the case of propylene glycol + 20% chloroform, where the scatter was 0.07). As a test of experimental accuracy, the autoprotolysis constant of ethylene glycol was determined and the value obtained, $pK_s = 15.76$, compares well with that determined by Zikolov *et al.*[3] of 15.72.

Determination of the dissociation constant of phthalic acid

For the determination of the acid dissociation constant of phthalic acid (H_2Ph) the following cell was used:

$$GE \| KHPh\text{–}C_2, (KCl + HCl)\text{–}C, SH | AgCl\text{–}Ag \quad (6)$$

Calculation of the concentrational constant was based on the equation

$$pK^{C}_{a(H_2Ph)} = -\log[SH_2^+] + \log \frac{[H_2Ph]}{[HPh^-]} \quad (7)$$

The concentrations of the phthalic acid species were calculated from the known stoichiometric amounts in the course of titration of hydrogen phthalate with hydrochloric acid. The concentration of the solvated proton (lyonium ion) was established on the basis of the titration curve after the equivalence point

$$-\log[SH_2^+] = \frac{E - E^0_a}{0.05916} \quad (8)$$

As before, the constancy of E^0_a was found to be satisfactory for each set of measurements, and the differences were of the same magnitude as those observed in the determination of the autoprotolysis constants. The values of the protolysis constants are presented in Table 2 for the same solvent mixtures as for the autoprotolysis constants, with the exception of the 21% water system, for which the titration curve was very indistinct.

DISCUSSION

The data in Table 1 indicate that pK_s for the autoprotolysis constant of propylene glycol (16.99) is more than one log unit larger than that for ethylene glycol ($pK_s = 15.72$). Addition of water shortens the acidity scale of propylene glycol, the effect being particularly strong for small percentages of water. The effect is more pronounced for propylene glycol than for ethylene glycol. Addition of 1% of water changes the pK_s value of the former by 0.54, but that of the latter by only 0.28. This suggests that removal of small amounts of water is more critical for propylene glycol than for ethylene glycol. It is further found that 20% of added chloroform or propan-2-ol decreases the autoprotolysis constant, whereas the same amount of acetone has practically no effect.

The acid–base properties of the solvents may be evaluated by comparison of the acidic dissociation constant of phthalic acid and the basic dissociation constant of the hydrogen phthalate ion. The latter is practically constant in propylene glycol–water mixtures and differs less from the value in aqueous solution ($pK_{HPh^-} = 11.05$) than does the value for ethylene glycol. This means that hydrogen phthalate is a stronger base in propylene glycol than in water, but is weaker in ethylene glycol by about 0.5 log unit. Hence propylene glycol is more acidic than water, being intermediate between water and ethylene glycol.

Addition of 20% of chloroform, or larger amounts of acetone, decreases the acidic properties of the solvent, but the effect of propan-2-ol is insignificant.

The values of the protolysis constants of phthalic acid indicate similarities in the properties of the solvent investigated and those of ethylene glycol, demonstrating that both glycols may be used in the titration of weak bases.

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THIN-LAYER CHROMATOGRAPHY OF ORGANIC SULPHATES, PHOSPHATES AND NITRATES

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Summary—Inorganic oxyanions and their corresponding organic esters, such as sulphates, phosphates and nitrates, have been separated by thin-layer chromatography on cellulose and silica gel plates.

Organic compounds which exist in natural products or biological materials are often extracted and isolated as sulphates[1–8] or phosphates.[9,10] Paper chromatography,[11,12] column chromatography,[13] thin-layer chromatography (TLC)[14] and, recently, high performance liquid chromatography (HPLC)[15] of these organic esters have been reported. We have already reported on the paper chromatography and TLC of inorganic anions and a new fluorescence-quenching detection method using the fluorescent aluminium–morin complex.[16]

In this paper, the TLC separation of organic sulphates, phosphates and nitrates is described.

EXPERIMENTAL

Reagents

Aqueous stock solutions (10 μg/μl) were prepared of all species except for the steroid nitrate, which was dissolved in chloroform.

Paper and thin-layer chromatography

Stationary phase. Commercially available chromatographic papers (Toyo Roshi for PC, No. 51A), precoated glass plates (Merck cellulose and silica gel precoated plates, without fluorescent indicator, for TLC) and Yamato REPLATE® silica gel/sintered glass plates were used. The paper and cellulose thin layers were used for the separation of inorganic anions, and the silica gel thin layers for organic compounds and their esters.

Mobile phase. Five solvent systems were used: (A) 28% ammonia solution–acetone–n-butanol (60:130:30, v/v), (B) n-butanol–acetic acid–water (3:1:1, v/v), (C) benzene–acetone (9:1, v/v), (D) chloroform–acetone (4:1, v/v) and (E) benzene–ethyl acetate (4:1, v/v). The inorganic anions were developed with the basic solvent system (A) and the organic esters with the other four.

Chromatographic procedure. One μl of each stock solution was applied with a microsyringe on the start points 5 cm (paper chromatography) or 2 cm (TLC) from the lower edge of each support. After air-drying, papers and plates were developed for a distance of 20 cm (paper chromatography) or 10 cm (TLC) in a cylindrical or rectangular chamber with saturated atmospheres (ambient temperature *ca.* 25°, relative humidity 55–65%). The developed chromatograms were air-dried and, if necessary, heated in an electric oven at 100–110° for 3–5 min.

Detection. The fluorescent morin–aluminium complex[16] was used for detection. It was prepared by dissolving 5 mg each of aluminium chloride and morin in a mixture of 10 ml of 30% acetic acid, 20 ml of 98% ethanol and 20 ml of water. The developed chromatogram, sprayed with this fluorogen, was viewed under ultraviolet light (365 nm). Darks spots of the anions and esters appeared on the bright greenish-yellow fluorescent background. Borate and silicate do not quench the fluorescence, and were detected by other methods.[17–19]

RESULTS AND DISCUSSION

Separation of inorganic oxyanions

The hR_F values (*i.e.*, $100 \times R_F$) and quenching effects of these anions are shown in Table 1. Borate and tetraborate were separable. Phosphate and sulphate gave extremely low hR_F values, and the nitrate anion a much higher value.

Table 2 indicates the relationships between the electronic charges and TLC hR_F values of the oxyanions, showing that the hR_F values become larger as the electronic charge of the central atom (A) or the bond length (A–O) decreases.

Separation of organic phosphate, sulphate and nitrate esters

Steroid esters. Cholesteryl-3-*O*-sulphate [mobile phases (B) and (C)] and dehydroisoandrosterone sulphate [mobile phases (B) and (D)] were chromatographed on silica gel sintered plates. Both moved from the start in acidic mobile phase (B), but not in the neutral mobile phases (C) and (D), presumably owing to strong adsorption onto the silica

Table 1. Cellulose thin-layer chromatography of inorganic oxyanion*

Oxyanion	hR_F value	Fluorescence quenching colour†
PO_4^{3-}	0	violet
$B_4O_7^{2-}$	5	§
SO_4^{2-}	5	violet
CrO_4^{2-}	6	violet
$Cr_2O_7^{2-}$	9	violet
IO_4^-	12	violet
IO_3^-	14	violet
BO_3^{3-}	15	§
SiO_3^{2-}	16	‡
ClO_2^-	35	yellow
BrO_3^-	43	violet
NO_2^-	55	violet
NO_3^-	60	violet
ClO_3^-	63	yellow
ClO_4^-	80	yellow

* Stationary phase, Merck TLC glass plate cellulose; mobile phase, 28% ammonia solution–acetone–*n*-butanol (60:130:30, v/v).

† Aluminum–morin fluorescent complex.

§ Morin–oxalic acid or curcumin–oxalic acid.

‡ Ammonium molybdate.

Table 2. Electronic charges, bond lengths and TLC hR_F values of inorganic oxyanions

Anion	Electronic charge of centre atom*	Bond length, (A–O), Å*	TLC hR_F value†
ClO_2^-	+0.38	1.57	35
ClO_3^-	−0.73	1.46	65
ClO_4^-	−0.90	1.44	80
PO_4^{3-}	+0.85	1.54	0
SO_4^{2-}	+0.29	1.49	5
NO_3^-	—	1.22	60

* L. Pauling, *The Nature of the Chemical Bond*, (1960, Cornell University Press), A = Cl, P, S and N; O = oxygen.

† TLC conditions as in Table 1.

gel thin-layer containing soda-lime glass powder. The hR_F values were small compared with those of the free steroids [cholesterol 70 in (B), 43 in (C); sulphate 54 in (B), 0 in (C); dehydroisoandrosterone 73 in (B), 54 in (D); sulphate 37 in (B), 0 in (D)].

The steroid nitrate moved smoothly even in the neutral mobile phase (E). Its hR_F value was slightly smaller than that of the steroid itself.

These mobilities are consistent with those of the sulphate and nitrate anions described above.

Sugar esters. Table 3 shows the hR_F values of hexose phosphates and free hexose on the silica gel sintered plates (REPLATE) and Merck silica gel glass plates (MS). The hR_F values on REPLATE were larger than those on MS.

Table 5. TLC of nucleotides on PEI cellulose sintered sheet*

Compound	hR_F value
Adenosine-5′-monophosphate	55
	ΔhR_F 25
Adenosine-5′-diphosphate	30
	ΔhR_F 23
Adenosine-5′-triphosphate	7

* Impregnated with 1% PEI (mass 3×10^4–4×10^4) hydrochloride aqueous solution.

† Developed with 1.0*M* LiCl, 10 cm/60 min; detection at 254-nm with Al–morin.

The difference in hR_F values (ΔhR_F, 38) between fructose and its 1,6-diphosphate on a REPLATE was about twice that (22, 14) between fructose and its 1- or 6-monophosphate, showing the additivity of ΔhR_F values for mono- and diphosphates.

Table 4 gives the hR_F values of three kinds of hexose and their sulphates on a REPLATE. Additivity of ΔhR_F values was observed as in the case of hexose phosphates.

Adenosine phosphates. Table 5 describes thin-layer chromatographic separation of three kinds of adenosine phosphate (AMP, ADP and ATP) on polyethyleneimine (PEI) cellulose–polyethylene sintered sheets.[20] In this case also, the hR_F values decreases as the number of phosphate groups attached to adenosine increases. As PEI cellulose is an anion-exchanger, sorption between the substrate (or

Table 3. TLC of sugar phosphates on silica gel plates

Hexose phosphate*	hR_F values† REPLATE	ΔhR_F	MS	ΔhR_F
Glucose	73 ± 3	23	30 ± 1	21
Glucose-1-phosphate	50 ± 2	18	9 ± 2	20
Glucose-6-phosphate	55 ± 3		10 ± 1	
Fructose	73 ± 2	22	33 ± 1	23
Fructose-1-phosphate	51 ± 2	14	10 ± 1	21
Fructose-6-phosphate	59 ± 4	38	12 ± 1	28
Fructose-1,6-diphosphate	35 ± 3		5 ± 2	

* Extra pure reagents, Wako Chemicals.

† Developer n-BuOH–AcOH–H_2O (3:1:1); detection, Al–morin reagent followed by conc. sulphuric acid. Development 10 cm in 2.0 hr (REPLATE), 2.5 hr (Merck silica gel glass plate), $n = 5$.

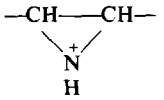
Table 4. TLC of sugar sulphates on silica gel plates

Hexose sulphate*	hR_F values† REPLATE	ΔhR_F	MS	ΔhR_F
Glucose	72	10	27	10
Glucose-6-sulphate	62	17	17	17
Glucose-1,6-disulphate	55		10	
Galactose	72	11	28	12
Galactose-6-sulphate	61	21	16	18
Galactose-1,6-disulphate	51		10	
Fructose	71	8	32	11
Fructose-6-sulphate	63	15	21	9
Fructose-1,6-disulphate	56		12	

* Synthesized by the method of Soda, *Nippon Kagaku Zasshi*, 1940, **61**, 683.

† Conditions as in Table 3.

the phosphate anion) and the stationary phase (the weak basic



is more evident than in the partition chromatography of the inorganic and organic anions described above.

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ANNOTATIONS

CONTAMINATION WITH CADMIUM FROM MICROPIPETTE TIPS

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Summary—Contamination by cadmium from micropipette tips from two different manufacturers was tested. Tips were washed with two different acids and the washing solutions were analysed by atomic absorption (graphite furnace). The washed tips were controlled by analysing pure acids and were found decontaminated. Clear contamination was found in yellow Eppendorf pipettes, which varied according to the consignment. The decontamination of disposable micropipette tips is emphasized when trace metal contamination should be avoided.

A literature survey indicated that there are not many references concerning contamination with metals from disposable micropipette tips. However, the rapidly expanding use of these tips and the sensitivity of modern analytical methods warrant investigation of the possibility of such contamination. For example, zinc, iron and calcium have been warned about and rinsing of the tips with 1*M* hydrochloric acid and water has been recommended. When determining micro-amounts of cadmium in dry-ashed human milk samples by graphite-furnace atomic-absorption spectrometry, we found it impossible to obtain reproducible signals, which varied significantly from one to another. The volume pipetted was 20 μl and a manual pipetting procedure was used. The pipette tips were, as usual, rinsed several times with the sample liquid before use. After some experiments we suspected contamination caused by the pipette tips. Twelve microlitre pipette tips from the two manufacturers were left in 50 ml of 2*M* hydrochloric acid overnight. The inside of the tips was also in contact with the acid. Next day the tips were rinsed several times with demineralized water and dried at room temperature before use. Three successive portions of 6*M* hydrochloric acid were introduced into the furnace with the same unwashed tip. The procedure was repeated with 2*M* hydrochloric acid. The acid used for soaking the tips was analysed three times, decontaminated tips being used to introduce it into the furnace.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 300 atomic-absorption spectrometer equipped with a deuterium background-corrector, HGA-74 graphite cell, HGA-2100 controller unit, Servogor Model RE 511 recorder and cadmium hollow-cathode lamp were used. The purge gas used was argon. The operating parameters were according to the manufacturers' manual. An Eppendorf 20-μl micropipette was used with yellow micropipette tips (for 5–100 μl pipettes, Eppendorf Gerätebau Netheler + Hinz GmbH) and Finnpipette tips (Labsystems Oy, Finland).

Reagents

Hydrochloric acid (Merck "Suprapur") solutions (2*M* and 6*M*) were made by diluting with dis-

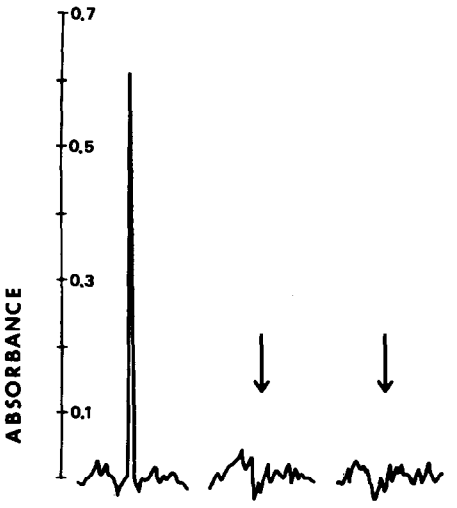

Fig. 1. Three 20-μl aliquots of 6*M* HCl introduced into the graphite furnace with the same unwashed pipette tip.

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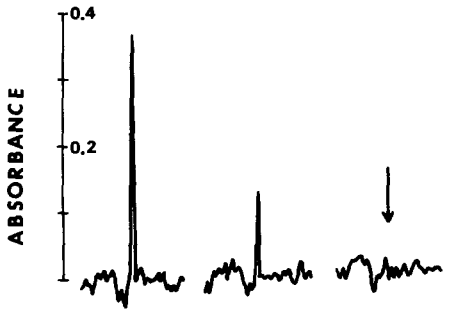

Fig. 2. Three 20-μl aliquots of 2*M* HCl introduced into the graphite furnace with the same unwashed pipette tip.

tilled and demineralized water (Santasalo Oy, Finland and Millipore Co., Super-Q System).

Standard cadmium solutions were prepared from 1000 μg/ml stock solution (Titrisol, Merck) on the day of use.

Procedure

Washing solutions and clean acids (20-μl portions) were pipetted manually into the graphite furnace with unwashed and with decontaminated pipette tips, then dried, ashed and atomized as usual. The argon purge gas was used in the continuous flow mode and ordinary graphite tubes were used. The recorder senstivity

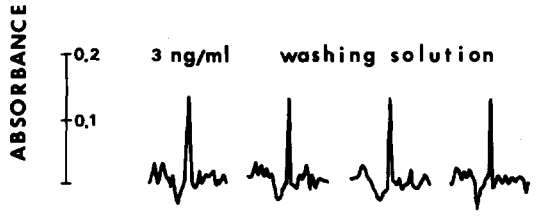

Fig. 3. Three aliquots of the acid washing solution (50 ml of 2*M* HCl) used for twelve micropipette tips, compared with a standard containing 3 ng/ml and pipetted with a decontaminated tip.

was 5 mV and the chart-speed 120 mm/min. The absorbance values are seen in the figures.

RESULTS AND DISCUSSION

When 20-μl samples of 6*M* hydrochloric acid were introduced with an unwashed Eppendorf pipette tip three times in succession, diminishing signals for cadmium were obtained. The first sample was strongly contaminated with cadmium and the effect disappeared in the next two. In the case of 2*M* hydrochloric acid the effect was similar, but decontamination of the tip took longer. The height of the peak depended not only on the concentration of acid used, but also to some extent on the time that the acid stayed in the tip. The solution (50 ml of 2*M* hydrochloric acid) used to wash the twelve micropipette tips was found to have a cadmium concentration of about 3 ng/ml. When the washed tips were used to pipette pure 2*M* and 6*M* hydrochloric acid they were found to have been decontaminated. The whole procedure was repeated with nitric acid ("Suprapur", Merck) and similar results were obtained. Another consignment of Eppendorf tips was tested as above and again found to be contaminated with cadmium, but not so strongly. No contamination was found in Finnpipette tips.

When micro-amounts of cadmium are to be determined and disposable pipette tips are used, the tips must be decontaminated by washing with an acid solution, *e.g.*, overnight with 2*M* hydrochloric acid. The cadmium contamination of the Eppendorf tips may be due to the yellow pigment of their casting. Other possible contaminants were not investigated.

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PHOTOMETRIC DETERMINATION OF COBALT WITH NITROSO-R-SALT

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Summary—The chelate is quantitatively formed only in the pH range 6.5–7.5. Despite the large stability constant, a large excess of reagent is required to suppress interferences. The most suitable wavelength for the photometric measurement is 500 nm, where the molar absorptivity is 1.607×10^4 l.mole^{-1}.cm^{-1}. The procedure given allows determination of 8×10^{-4}% Co in a 1-g sample. The standard deviation for cobalt is 2.1 μg/100 ml ($f = 19$). Applications to analysis of iron and steel, nickel, copper, ores and silicates are given.

Among the nitrosonaphthols, which are frequently used for the photometric determination of cobalt, nitroso-R-salt has the advantage of water solubility and therefore simplicity of use.[1–6] It is felt, however, that none of the known procedures is sufficiently versatile, simple, and described in detail to fulfil the requirements of undergraduate and graduate teaching of analysis.[3] Further, they all suffer from lack of thorough statistical characterization, and the wide variety of pH-values, wavelengths, and reagent concentrations suggested in the literature suggest that it might be advisable to re-examine these parameters.

The cobalt chelate of nitroso-R-salt is formed only above pH 3–4, but once formed it resists even hot dilute mineral acids. This allows selective destruction of the chelates of other metals, and thus elimination of many interferences. At the absorption maximum of the chelate the reagent blank is so high that it is necessary to make the measurement at a longer wavelength. The decrease in sensitivity is outweighed by the simultanous decrease in absorbance of coloured cations, such as those of Fe(III), Cr(III), Ni(II), see Fig. 1. A sufficiently large excess of reagent is important to suppress interferences. Reducing and oxidizing agents must be absent.

EXPERIMENTAL

Range of applications

The following standard procedure can be applied directly to steel and iron samples containing not less than 0.2% cobalt and not more than 1 or 2% chromium. Otherwise a zinc oxide separation will be necessary. Ores, nickel alloys, and light metals can be analysed without special precautions, if they contain at least 0.05% Co. For lower concentrations it is necessary to use specialized matrix separations.

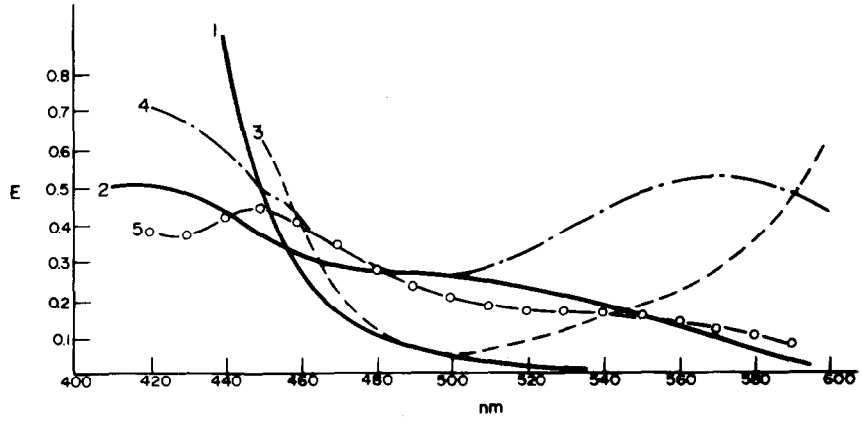

Fig. 1. Absorption spectra: 1, reagent blank; 2, Co chelate, 1 ppm Co (reagent concentration only 0.02%); 3, 1000 ppm Ni(II); 4, 1000 ppm Cr(III); 5, 1000 ppm Fe(III); No. 1 measured against water, Nos. 2–5 against reagent blank.

Reagents

Nitroso-R-salt solution, 0.5%. Can be kept for months if stored in a dark bottle.

Citrate solution, 40%. Dissolve 40 g of sodium citrate in water, adjust to pH 7.0, and dilute to 100 ml.

Indicator solution. A 0.1% solution of Bromothymol Blue in 50% aqueous ethanol.

Sodium hydroxide solution, 10%. Store in a plastic dropping bottle.

Standard cobalt solutions. (*a*) Dissolve 100 mg of cobalt metal in nitric acid, boil to expel nitrous oxides, and dilute to 1000 ml. (*b*) Dehydrate $CoSO_4.7H_2O$ at 400–500°. Dissolve 263.0 mg of the anhydrous $CoSO_4$ in water and dilute to 1000 ml. In both cases 1 ml contains 100 μg of Co. For use prepare a fresh 10-μg/ml solution daily.

Standard procedure

Transfer an aliquot of the sample solution containing from 40 to 400 μg of cobalt to a 150-ml beaker. Add 5 ml of citrate solution and 0.5 ml of indicator solution. Neutralize with sodium hydroxide until the indicator turns blue (pH 7.0–7.3). If necessary prepare a mixture of 20 ml of water + 5 ml citrate solution + 0.5 ml of indicator as a colour standard. Small amounts of a precipitate do not interfere. Add exactly 10 ml of nitroso-R-salt solution and bring the mixture just to the boil. Then add 5 ml of half-conc. (34%) nitric acid (measuring cylinder) and boil for 1 min. Erratic boiling times should be avoided. Cool to room temperature, transfer to a 100-ml standard flask and make up to the mark with water. Prepare a reagent blank similarly. Measure the absorbance against the blank within 30 min, using 1-cm cells. The most suitable wavelength is 500 nm, or the lines at 492 nm (Hg) or 509 nm (Cd) can be used. With the 546 nm (Hg) line or the Zeiss filter S 52, the working range is 60–600 μg of Co. By measurement in 5-cm cells, a concentration of about 5 μg/100 ml can be determined, but to obtain sufficient precision considerable practice is required.

To construct the calibration curve, use the standard solution and follow the procedure described above.

Procedure for nickel alloys

Down to 0.05% Co can be determined by the standard procedure, after dissolution of the sample in acid. If samples weighing more than 200 mg are required, nickel will interfere by consuming reagent, and also by the colour of the nickel ions. In this case the amount of nitroso-R-salt must be doubled. In addition, the colour of the nickel ions must be compensated for by treating an equal amount of the sample solution by the standard procedure, but with omission of the nitroso-R-salt. The absorbance is measured at the wavelength to be used, against water as a blank, and subtracted from the cobalt absorbance.

Procedure for copper alloys

Dissolve the sample in nitric acid, add some sulphuric acid and heat to fumes. Then remove the bulk of the copper by electrolysis, less than 2 mg of copper being harmless. Precipitation with hydrogen sulphide may also be applied;[8] in that case wash the sulphide with H_2S-water, boil to expel hydrogen sulphide, and then oxidize with nitric acid. Then apply the standard procedure.

Procedure for silicates

Glass, enamel, cement, *etc.* must be very finely ground. Treat the sample with hydrofluoric and sulphuric acids, heat to fumes, cool, take up in water, filter, and apply the standard procedure.

Procedure for steel and iron ores

Materials containing less than 0.2% cobalt and/or more than 2% chromium require a hydrolytic separation.[4,7] This will remove Fe, Cr, Ti, V, Mo, W, Nb, Zr *etc.* Since a small amount of the cobalt may be co-precipitated, the standard addition method should be used.

Dissolve steel samples in hydrochloric acid, then oxidize with nitric acid. Decompose silicate materials with hydrofluoric and sulphuric acids, heat to fumes, cool and take up the residue with nitric acid. In both cases dilute to the mark in a small standard flask. Transfer aliquots of this solution, conveniently containing 100–500 μg of Co, to 150-ml beakers, and spike one or two of them with standard amounts of 300 or 400 μg of Co. If the solution is strongly acidic, neutralize with sodium hydroxide until the first persistent precipitate appears, then add some drops of hydrochloric acid to redissolve it. Heat to just below the boiling point and cautiously add zinc oxide until a small amount remains undissolved. Boil, cool, transfer to a 100-ml standard flask, and make up to the mark and mix thoroughly. It will often be sufficient to pipette an aliquot of the turbid solution after the bulk of the precipitate has settled. Alternatively, centrifuge or pour through a dry filter, discard the first drops of the filtrate and then take an aliquot for analysis.

RESULTS AND DISCUSSION

Various wavelengths for the photometric measurement are recommended in the literature.[1] Figure 1 shows the optical properties of the system. The most suitable wavelength is 500 nm, where interference by the colour of nickel and chromium is minimal. The absorption by iron(III) and the oxidized excess of reagent is very small at 500 nm. The measurement at the absorption maximum of the chelate is precluded if the reagent absorbance is too high, but decreasing its concentration would increase the risk of interference.

The cobalt chelate is usually formed in an acetate-buffered medium at about pH 5,[4,5,9,10] occasionally at pH 8.[11] Figure 2 shows the absorbance stability to be maximal at pH 6.5–7.5. Above pH 8 and below pH 6 the absorbance decreases sharply. The procedure described here makes use of a concentrated citrate buffer with a pH of 7.0, which simultaneously acts as an auxiliary complexing agent. An indicator is sufficient to control the pH, since small deviations from the optimal value (±0.5 units) are without influence on the results.

The cobalt chelate is very stable, and under mild conditions the stoichiometric amount of reagent is sufficient for its quantitative formation.[5] If, however, the solution is treated with nitric acid to decrease the blank and destroy the chelates of other metals, a large excess of nitroso-R-salt is necessary: see Fig. 3. A further increase in reagent concentration is advisable, since some species, *e.g.*, Ni(II) and Cr(III), interfere by consuming reagent. Though their chelates are destroyed by nitric acid, a too small initial excess may not leave enough reagent for complete chelation of cobalt.

Interferences

The amount of sample used must not contain more than the amounts (mg) of other elements given in parentheses: Al, Ca, Mg, Zn (100–200); Ni (50); Fe, Ti (20); Mn, W (10); V, Mo (5); Cr, Cu (2). About 10

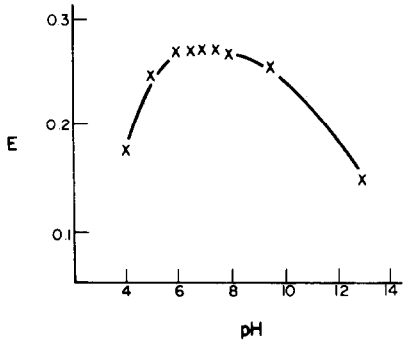

Fig. 2. Optimum pH-range for formation of the Co chelate.

mg of Cr(III) is tolerable if the boiling time is extended from 1 to 5 min, provided that this time is also used for the calibration. Iron must be in the tervalent state; nitric acid should be used for oxidation. The amount of citrate added may be doubled, if necessary, to prevent precipitation of hydroxides.

Statistical evaluation

Correlation analysis shows the strict linearity of the calibration curve (significance level $P = 99.9\%$). Regression analysis of the expression $y = ax + b$ yields a molar absorptivity of $\epsilon = 1.607 \times 10^4$ l. mole^{-1}. cm^{-1} at 500 nm, measured with a half-bandwidth of 0.36 nm, standard deviation 77 l. mole^{-1}. cm^{-1} (19 degrees of freedom). It is not probable that $b \neq 0$ ($P = 95\%$; $f = 19$), *i.e.*, the calibration graph passes exactly through the origin. Hence the Lambert–Beer law is strictly obeyed, and the standard addition method can be applied if necessary. Determinations of standard cobalt solutions, steels and silicates, without ZnO separation, show a standard

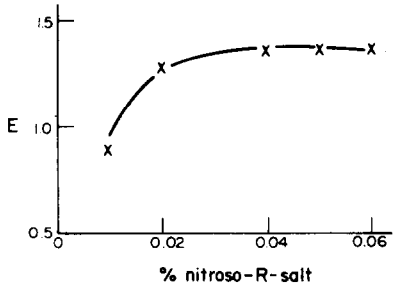

Fig. 3. Amount of reagent required.

deviation of 2.1 μg/100 ml (19 degrees of freedom), so the confidence interval of the mean of $M = 2$ runs is $\Delta\bar{x}_2 = \pm 4.3$ μg/100 ml at the 99% level. Following the definition by Gottschalk,[12] the most suitable one for photometry, the determination limit (not detection limit!) is $c = \sqrt{2}ts/\sqrt{M} = 8.3$ μg/100 ml ($M = 2$; $P = 99.9\%$). The absorbance at this limit is 0.023 in 1-cm cells. With a 1-g sample for each run, $8 \times 10^{-4}\%$ Co (8 ppm) can be determined. Applying the criterion given by Eckschlager,[13] the permissible difference between the absorbances for a duplicate run is 0.016 (for 1-cm cells), at the sufficient significance level of $P = 95\%$. Any larger difference points to a doubtful value and demands a further run for decision. The analysis of steels, ores and nickel alloys, including the ZnO separation procedure, has an absolute standard deviation of 0.0041% Co ($f = 14$) in the range 0.025–0.5% Co. The blank absorbance for samples without interfering constituents is 0.075, measured at 500 nm in 1-cm cells against water; its standard deviation, drawn from homogeneous data, is 0.003 ($f = 12$).

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PHOSPHORESCENCE OF ADSORBED MOLECULES AT ROOM TEMPERATURE—THE FIRST OBSERVATIONS?*

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Summary—The room-temperature phosphorescence of molecules adsorbed on cellulose and other supports seems to have been "discovered" no less than four times.

The current interest in analytical applications of the room temperature phosphorescence (RTP) of adsorbed molecules (principally on cellulose) is undoubtedly due to Schulman and Walling's report of their work in 1972.[1] Although at that time they could find no comparable observations in the literature, several did in fact exist. One of these, by Roth,[2] has recently been acknowledged by Schulman and Parker.[3]

The first observation of which we are aware was made by Millson in 1944,[4] but apparently was not widely publicized before 1954.[5] He observed that along with a variety of other fibres various cottons phosphoresced, evidently at room temperature, particularly when "bone dry". We can confirm that the effect is readily reproduced. In view of the more recent work it is apparent that the phosphorescence must be due to contaminants adsorbed on the cotton. Highly purified cotton does not exhibit the effect.

The second observation was by Brown in 1958.[6] He wrote: "When viewed on a paper chromatogram in ultraviolet light, 2-mercaptonaphth[2,3]iminazole shows a brilliant yellow phosphorescence for several seconds after withdrawal of the light source. 2-Mercaptobenziminazole does not do this."

We have repeated the experiment with the naphthiminazole and can confirm Brown's observation, and that the phosphorescence shows a similar dependence on the experimental conditions as in the instances reported since. This includes the same requirement for the presence of water prior to dehydration of the adsorbate if a strong phosphorescence is to be seen.[7] It is not surprising that this compound was the first identified to give the effect. Its phosphorescence is outstandingly brilliant, and remains visible even after rehydration of the support. A phosphorescence is also obtained with non-hydroxylic supports, *e.g.*, poly(vinylpyrrolidone).

Until very recently, Roth's paper of 1967[2] had also been entirely overlooked. It should be noted that he reported a study of the RTP of no fewer than 29 compounds on several supporting media. Of these compounds, 17, including several acyl 2-naphthylamides, 1- and 2-naphthols, and 1,10-phenanthroline, were found to be sufficiently phosphorescent on cellulose surfaces to be detectable at microgram or submicrogram levels. L-Cystinyl di-2-naphthylamide was weakly phosphorescent, and the remaining compounds, including 8-hydroxyquinoline, folic acid, chrysene and fluorescein, were apparently non-phosphorescent. Polysaccharide matrices were found to be necessary: feebler phosphorescence signals were observed when the samples were adsorbed on a mixed starch–silica gel layer, and no phosphorescence was detected when silica gel or alumina surfaces were used. In all cases the phosphorescence could be seen over a period of several seconds after the removal of the exciting light source—a low-pressure mercury lamp. It is thus possible that other phosphorescences have been overlooked because the phosphorescence lifetimes were very short or the wavelength of the excitation light was inappropriate. Roth[2] emphasised the value of the technique as a simple, selective and non-destructive method for studying chromatograms and electropherograms. It is of interest that the use of strongly alkaline conditions[1] was apparently unnecessary. Also, although the chromatograms were studied after drying, there was no mention of the very rigorous drying normally used.

It is perhaps understandable that Brown's report[6] has until now been overlooked, as his observations were incidental to the main topic of his paper, and are not mentioned in the summary or in the relevant Chemical Abstract.[8] The content of Roth's paper[2] is, however, apparent from its title and also from the Abstract,[9] and it seems clear that he was the first to recognize the generality of the effect in an analytical context. However, both Millson[4] and Brown[6] have some claim for priority as both of them recognized and used the effect analytically within the fields in which they were working.

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COMPARAISON DE TROIS METHODES DE DOSAGE DU CUIVRE PAR ANALYSE STATISTIQUE

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Résumé—Trois méthodes de dosage du cuivre, parmi les plus fréquemment utilisées, et permettant des déterminations dans l'intervalle 0.5–10 μg/l., ont été comparées par analyse statistique. La détermination des courbes d'étalonnage a été réalisée à l'aide de l'analyse de régression, et les intervalles de confiance ont été calculés, permettant de déduire un indice de précision pratiquement constant pour chacune des courbes d'étalonnage. La méthode de dosage par absorption atomique apparait la plus recommandable, compte-tenu du gain de temps qu'elle procure lors d'une étude générale portant sur plusieurs métaux.

La sélection d'une méthode d'analyse adéquate permettant de mesurer avec une précision suffisante les teneurs de traces de cuivre dans des échantillons d'eau doit également tenir compte de critères fondamentaux tels que sensibilité, spécificité, simplicité d'utilisation et rapidité d'exécution.

Trois méthodes de dosage du cuivre, parmi les plus fréquemment utilisées, et permettant des déterminations dans l'intervalle 0.5–10 μg/l. ont été sélectionnées: méthode M_1 utilisant le pouvoir complexant du diéthyldithiocarbamate de sodium (SDDC);[1] méthode M_2 avec le 2,2'-diquinolyle;[2] méthode M_3 faisant intervenir la formation de chélate avec l'ammonium 1-pyrrolidinecarbodithioate (APDC).[3] Les mesures spectrophotométriques d'absorption de la lumière ont été effectuées avec un appareil Unicam SP 1800, respectivement à 436 nm pour M_1 et 540 nm pour M_2. Les mesures d'absorption atomique ont été faites sur un appareil Perkin-Elmer, modèle 306 à 325 nm pour M_3.

Le but de ce travail a été de comparer les précisions de ces trois méthodes au moyen de l'analyse statistique.

RESULTATS ET DISCUSSION

La détermination des courbes d'étalonnage du cuivre (absorbance en fonction de la concentration) est réalisée à partir des données expérimentales à l'aide de l'analyse de régression.[4,5] Huit valeurs prédéterminées de la concentration en cuivre (variable indépendante) sont utilisées pour évaluer les variations de l'absorbance (variable dépendante) suivant la méthode de dosage employée. Bien que deux, parfois trois lectures aient été effectuées sur certains sous-échantillons d'un même échantillon, une seule valeur a été retenue pour chacune des 24 (8 × 3) mesures d'absorbance.

Pour un seuil de probabilité de 95%, l'hypothèse de l'homogénéité des variances résiduelles peut être acceptée pour les trois méthodes de dosage (test de Bartlett). Les courbes d'étalonnage ainsi déterminées sont linéaires dans l'intervalle étudié des valeurs de concentration étudié (test de linéarité). Le calcul du coefficient de corrélation entre la concentration de cuivre et l'absorbance a donné des valeurs hautement significatives pour chacune des trois méthodes de dosage. La valeur du coefficient de régression ou de proportionnalité (*b*, exprimé en unités d'absorbance par μg/l.) et celle de l'ordonnée à l'origine (*a*, exprimé en unités d'absorbance) correspondant à chaque méthode de dosage sont estimées suivant la méthode des moindres carrés. La précision avec laquelle ces coefficients sont

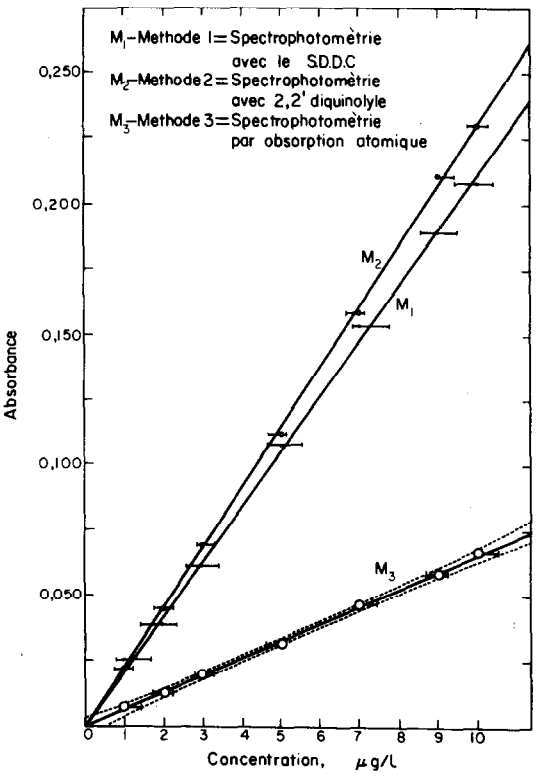

Fig. 1. Courbes d'étalonnage du cuivre déterminées selon la méthode des moindres carrés. Les équations des trois droites de régression estimées ont pour expression: (M_1) $y_1 = 0{,}00025 + 0{,}02105x$; ($M_2$) $y_2 = -0{,}00094 + 0{,}02309x$; ($M_3$) $y_3 = 0{,}000117 + 0{,}00662x$. Pour plus de clarté, les limites de confiance à 95% ont été tracées en pointillés pour tous les points de la courbe M_3 seulement. Les points expérimentaux sont représentés par des symboles.

Tableau 1. Analyse de regression des courbes d'étalonnage et comparaison des trois méthodes d'analyse

	Concentration initiale x, $\mu g/l$.	Coefficient de corrélation	$a \pm ts(a)$	$b \pm ts(b)$	Concentration estimée, $x_0 \pm ts(x_0)$, $\mu g/l$.	Indice de précision, $\mu g/l$.	Sensibilité, $\mu g/l$.	Limite de détection, $\mu g/l$.
M_1	0	0,99904	0,0002 ± 0,0538	0,0211 ± 0,0009	−0,12 ± 0,50	±0,48	0,21	0,13
	1				1,21 ± 0,48			
	2				1,83 ± 0,47			
	3				2,92 ± 0,46			
	5				5,11 ± 0,46			
	7				7,24 ± 0,47			
	9				8,95 ± 0,50			
	10				9,85 ± 0,51			
M_2	0	0,99974	−0,0009 ± 0,0029	0,0231 ± 0,0005	0,04 ± 0,26	±0,25	0,19	0,15
	1				0,99 ± 0,25			
	2				1,99 ± 0,24			
	3				3,07 ± 0,24			
	5				4,89 ± 0,24			
	7				6,88 ± 0,24			
	9				9,13 ± 0,26			
	10				9,99 ± 0,27			
M_3	0	0,99971	0,0001 ± 0,0009	0,0066 ± 0,0001	−0,01 ± 0,27	±0,26	0,66	0,10
	1				1,11 ± 0,26			
	2				1,94 ± 0,26			
	3				3,00 ± 0,25			
	5				4,89 ± 0,25			
	7				7,08 ± 0,26			
	9				8,89 ± 0,27			
	10				10,09 ± 0,28			

La valeur critique de la variable t de *Student* à $v = n - 2 = 6$ degrés de liberté au niveau de confiance $\alpha = 0{,}05$ (bilatéral) est $t = 2{,}447$.
L'équation de la droite de régression est de la forme y (absorbance) $= a + bx$ (concentration).

connus est évaluée statistiquement à partir de la variation résiduelle, c'est-à-dire de la dispersion (écart type) des mesures expérimentales d'absorbance autour de la droite de régression; les valeurs des concentrations standards sont admises avec une erreur négligeable.

La comparaison des courbes analytiques, prises deux à deux, s'effectue à l'aide du test de *Student*. Les tests de signification appliqués au paramètre *a* montrent que les trois droites d'étalonnage passent par l'origine, les limites de l'intervalle de confiance encadrant la valeur zéro (Tableau 1). Les pentes des trois droites s'avèrent être significativement différentes entre elles et significativement différentes de zéro. Le non recouvrement des intervalles de confiance calculés pour les trois coefficients de régression confirme ce résultat (Tableau 1). L'intervalle de confiance correspondant à chaque valeur estimée de la concentration (Tableau 1) est représenté par un segment de droite horizontal (Fig. 1). Il est possible de déduire un indice de précision pratiquement constant pour chacune des courbes d'étalonnage (Tableau 1). La courbe la plus précise (M_2) étant prise comme courbe de référence,[6] l'exactitude relative des droites de calibration est évaluée en termes de régression. Il apparaît ainsi que les trois méthodes sont sensiblement identiques du point de vue de l'exactitude relative. La présente analyse de régression ne permet pas de mettre en évidence des différences importantes entre les mesures de concentration déduites de l'une ou l'autre des trois méthodes de dosage envisagées.

CONCLUSION

La sensibilité des méthodes M_1 et M_2 (environ 0,20 μg/l.) est nettement supérieure à celle qui est obtenue avec la troisième méthode (0,66 μg/l.) et se traduit par des droites de calibration de pentes différentes (Fig. 1). Les limites de détection se situent dans le même ordre de grandeur (0,15 μg/l.) et ne permettent pas de porter un jugement sélectif en faveur de l'un ou l'autre des trois modes opératoires. L'indice de précision déduit des limites de confiance pour chacune des courbes montre que la première méthode d'analyse conduit à des résultats moins précis que les deux autres. Toutefois, les trois dosages s'avèrent pratiquement équivalents du point de vue de l'exactitude relative, avec des coefficients de corrélation proche de l'unité. Les conclusions générales suivantes peuvent être déduites:

Méthode M_1 *(SDDC).* Bonne sensibilité; précision médiocre. Son utilisation judicieuse se limiterait à la détermination de teneurs supérieures ou égales à 10 μg/l.

Méthode M_2 *(2,2'-diquinolyle).* Très longue du point de vue manipulation. Excellentes valeurs pour la précision et la sensibilité.

Méthode M_3 *(absorption atomique).* Très bonne précision, sensibilité médiocre. L'intérêt principal réside dans le fait que cette méthode peut permettre le dosage de plusieurs métaux à partir de la même solution,[3] en mesurant l'absorbance de la phase organique à diverses longueurs d'onde. C'est cette dernière méthode qui semble la plus intéressante et la plus recommandable, surtout compte-tenu de son aspect pluraliste et du gain de temps qu'elle procure ainsi lors d'une étude générale portant sur plusieurs métaux.

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Summary—Three methods commonly used for copper measurements in the range 0.5–10 μg/l. were compared by statistical analysis of the data. Regression analysis was applied to the calibration curves, and confidence intervals were calculated, providing a constant index of precision. The atomic-absorption method seems to be the best choice, especially because it permits much saving of time when several metals are to be determined in the same sample.

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THE ELECTROCHEMICAL REACTION OF NITRATE IN *N,N*-DIMETHYLFORMAMIDE

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Summary—Polarography, cyclic voltammetry and controlled-potential coulometry were used to study *N,N*-dimethylformamide solutions of nitrate. Nitrate is reversibly reduced in a one-electron step to NO_2. The diffusion coefficient of nitrate was polarographically estimated to be 4.6×10^{-6} cm^2/sec. Polarography in dimethylformamide was found to be a convenient method of analysis for nitrate in a solid fertilizer.

Since the original study by Tokuoka,[1] considerable interest has been shown in the polarographic reduction of nitrate in various aqueous solutions.[2] Controlled-potential coulometry of nitrate at a mercury cathode in aqueous solution has been done by Collat and Lingane.[3] The potential of the nitrate reduction wave was found to be dependent upon the cation present in aqueous solution. In view of the relatively high solubility of several nitrate salts in dimethylformamide (DMF)[4] and their consequent potential importance, the present electrochemical study was undertaken.

EXPERIMENTAL

Chemicals

N,N-Dimethylformamide (Baker Analyzed Reagent) was stored under a dry nitrogen atmosphere and used without further purification. A 0.1*M* solution of "Baker"-grade tetrabutylammonium perchlorate (TBAP; J. T. Baker) was used as the supporting electrolyte. Reagent-grade silver nitrate was used for the reference electrode filling solution. Potassium nitrate (Mallinckrodt, analytical reagent grade) and other reagent-grade nitrate salts were used as received. Linde dry-grade nitrogen was used to deaerate samples prior to electrochemical study and to protect the solvent and cell solutions from the atmosphere.

Apparatus

A model 174a Polarographic Analyzer (Princeton Applied Research) was used with an Omnigraphic 2000 x–y recorder (Houston Instrument) for voltammetry or with an Omniscribe strip chart recorder (Houston Instrument) for controlled-potential coulometry. A silver–0.010*M* silver nitrate reference electrode and a platinum auxiliary electrode were used. The silver nitrate reference solution was prepared daily. All reported potentials are relative to the silver–silver nitrate reference electrode. The working electrode was a Metrohm hanging mercury drop electrode (h.m.d.e.) for cyclic voltammetry, a dropping mercury electrode (d.m.e.) for polarography, and a mercury pool for controlled-potential coulometry. All polarographic current measurements were made at the top of the undamped recorder traces.

The three-compartment, water-jacketed cell was maintained at 25.0°, unless otherwise indicated, for cyclic voltammetry and polarography. The two outer compartments in the cell were separated from the centre compartment by medium-porosity glass frits. The cell used for controlled-potential coulometry was a 100-ml tall-form beaker sealed with a rubber stopper containing fritted glass tubes for the auxiliary and reference electrodes, and a platinum electrode which provided electrical connection to the mercury pool working electrode. Controlled-potential coulometry was done at room temperature (24–26°).

RESULTS AND DISCUSSION

Preliminary polarographic studies with calcium nitrate, potassium nitrate and sodium nitrate revealed a single cathodic wave at the same potential for each salt. Potassium nitrate was chosen for the remainder of the studies because of its higher solubility in DMF.

Potassium nitrate in DMF had a single cathodic wave at a half-wave potential ($E_{1/2}$) of -2.463 ± 0.010† V (Fig. 1) for ten solutions of various concentrations between 1 and 11m*M*. The location of this wave corresponds to the location of the previously unexplainable wave observed after exhaustive reduction of the copper(II) in copper(II) nitrate solutions in DMF.[5]

The random variation in $E_{1/2}$ with concentration is attributable to slight daily variations in the reference electrode potential and other experimental parameters. A constant $E_{1/2}$ with changing concentration indicates diffusion control of a reversible electron

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† The uncertainties quoted are standard deviations.

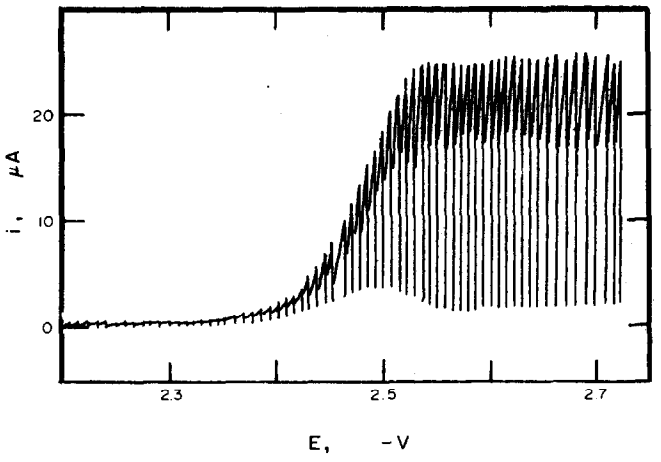

Fig. 1. A polarogram of 8.4 m*M* potassium nitrate in DMF.

transfer.[6] The temperature coefficient of the half-wave potential of 3.6m*M* nitrate, measured at 5° temperature intervals between 10° and 40°, was found to be +0.2 mV/deg. This value is within the expected range for a reversible electrode reaction.[7a] Plots of potential (E) as a function of $\log[i/(i_d - i)]$ were obtained for four samples of various concentrations. The slope of the resulting straight lines was −0.059 ± 0.003 V/decade. This value is identical to the theoretical slope for a reversible one-electron transfer.

The diffusion current (i_d) of the polarographic wave increased linearly with the square root of the corrected mercury column height (h_{corr}), and $i_d/h_{corr}^{1/2}$ decreased slightly with h_{corr} as expected for an electroactive species which obeys the Ilkovič and Koutecky equations.[7b] This is considered to be evidence of diffusion control of the height of the polarographic wave. The relative temperature coefficient of the diffusion current measured at seven temperatures from 10° to 40° was +1.0%/deg as compared to the theoretical value of about +1.3%/deg (in aqueous solutions).[7c] The closeness of the theoretical and observed temperature coefficients indicates the lack of partial or complete catalytic or kinetic control of the diffusion current, *i.e.*, the electroreduction does not involve any slow chemical steps.

Exhaustive controlled-potential coulometry of six potassium nitrate solutions at −2.7 V and one nitrate solution at −2.5 V yielded a calculated n of 1.03 ± 0.07 mole of electrons transferred for each mole of nitrate. Polarograms taken after each electrolysis contained no cathodic or anodic waves between 0 and −3 V.

The polarographic diffusion current increased linearly with increasing concentration (C) from 1.4 to 10.5m*M*. The slope of the i_d–C plot was used with the coulometrically and polarographically determined n of 1, the measured capillary characteristics, $m^{2/3}t^{1/6}$, of 1.86 $mg^{2/3}.sec^{-1/2}$, and the Ilkovič equation ($i_d = 708\ nD^{1/2}m^{2/3}t^{1/6}C$) to calculate a diffusion coefficient (D) for nitrate of 4.6×10^{-6} cm^2/sec.

Cyclic voltammograms recorded at the h.m.d.e. at scan-rates between 0.020 and 1 V/sec contained a single cathodic peak at about −2.5 V. Upon scan reversal, a normal anodic peak was observed at about −2.44 V and one or more "spiked" peaks could be observed at potentials more positive that that for the normal anodic peak. As the scan-rate was increased, fewer spiked peaks were observed and their potentials became more positive until at scan-rates of 0.5 and 1 V/sec only the normal anodic peak was seen (Fig. 2). The cathodic peak potential remained constant with changing scan-rate, indicating a reversible, diffusion-controlled, electron transfer.[6] The difference in peak potential between the cathodic and anodic peaks increased from the reversible, one-electron-transfer value[8] of about 0.06 V at 0.020 V/sec to the less reversible value of about 0.085 V at 1 V/sec. Application of the diagnostic criteria of Nicholson and Shain[9] to the potassium nitrate cyclic voltammograms indicated a reversible electron transfer.

The available evidence indicates the reversible, single-electron reduction of nitrate in DMF. Given the experimental conditions, it is likely that the reduction product is an oxide. The only well-known oxides of nitrogen(IV) are NO_2 and N_2O_4.[10] Of these two possibilities, NO_2 is the logical reaction product since the electrochemical evidence indicates lack of both an electrochemical dimerization and an electron transfer followed by a chemical dimerization. Of course N_2O_4 could have been formed from a chemical dimerization after the electron transfer if the chemical reaction were too slow to affect the cyclic voltammetry results.

In an effort to confirm the identity of the reaction product, a mixture of NO_2 and N_2O_4, which had been generated by the addition of nitric acid to copper, was forced through an empty trap to remove any liquid and into the DMF solution. Prior to addition of the NO_2, cyclic voltammograms of the solution showed no peaks between −0.5 and −2.9 V. After addition of the NO_2 (and N_2O_4), the cyclic voltam-

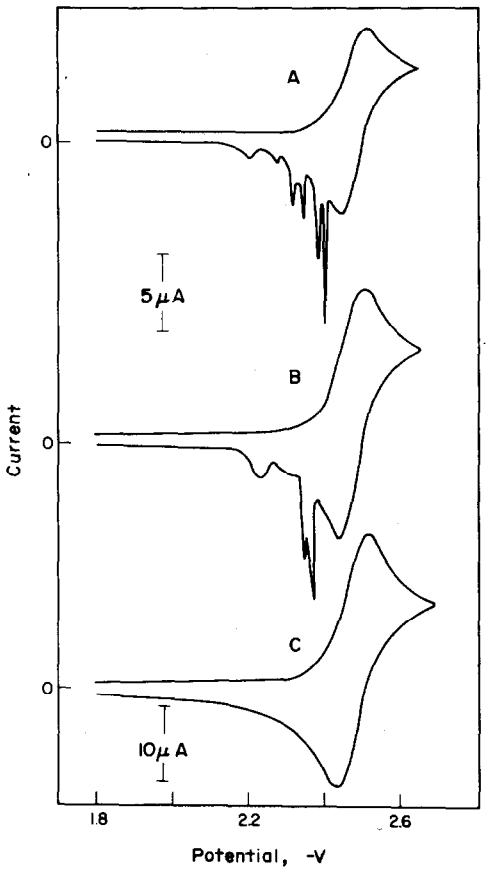

Fig. 2. Cyclic voltammograms of 1.4m*M* potassium nitrate in DMF. (A) 0.05 V/sec; (B) 0.1 V/sec; (C) 0.5 V/sec.

mograms contained two anodic peaks at −2.44 and −2.7 V, and cathodic peaks at −2.2, −2.5 and −2.8 V. The anodic peak at −2.44 V and the cathodic peak at −2.5 V have peak potentials corresponding to those observed for nitrate and consequently can be attributed to the oxidation of NO_2 (or N_2O_4) to nitrate followed by the reduction of nitrate to NO_2. This evidence strengthens the conclusion that NO_2 (or N_2O_4) is the electrochemical reduction product of nitrate.

When the cyclic voltammograms were recorded a second time in the same solution with the same mercury drop, the cathodic peaks at −2.2 and −2.8 V and the anodic peak at −2.7 V were observed to increase in height while the −2.44 V anodic peak and the −2.5 V cathodic peaks either remained at about the same height or showed a decrease in height. When the cyclic voltammograms were recorded a third time with a fresh mercury drop, the −2.2 and −2.8 V anodic peaks and the −2.7 V cathodic peak decreased in height. This evidence appears to indicate chemical reaction of the NO_2 or N_2O_4 with mercury from the electrode to yield a product or products with cathodic peaks at −2.2 and −2.8 V and with an anodic peak at −2.7 V. The identity of this product is at present unknown.

The "spiked" anodic peaks observed during cyclic voltammetry are probably due to the relatively slow chemical reaction of NO_2 to form a product which is anodically stripped from the electrode surface as it is formed. As the scan-rate was increased, less time was available for the chemical reaction to take place during the measurement, and consequently fewer spiked peaks were observed. Those peaks that were observed occurred at more positive potentials in order to allow enough time to elapse for the chemical reaction to take place. Since the reaction of NO_2 with mercury from the electrode yields a product with an anodic peak at about −2.7 V, it is possible that this product is responsible for the observed spikes.

It is difficult to write a balanced half-reaction for the electrochemical reduction of nitrate without using water. The water content of the DMF was found to be 0.02% (v/v) by Karl Fischer titrimetry. This corresponds to a solution which is about 10m*M* in water. Since the water concentration is greater than the nitrate concentrations used during most of this study, it is reasonable to assume that water can take part in the half-reaction and one possibility is

$$NO_3^- + H_2O + e^- = NO_2 + 2OH^- \quad (1)$$

It is interesting to note that although an anodic cyclic voltammetry peak was observed, no corresponding polarographic wave was seen after exhaustive controlled-potential coulometry of nitrate solutions. A reasonable explanation for this observation is the escape of the reaction products as a gas during the relatively long times required for each electrolysis (30–45 min). Conditions were ideal for escape of gaseous products since rapid stirring and a high flow rate of nitrogen over the solution were maintained during each electrolysis.

Polarography in DMF solution cannot be recommended as a method of analysis for nitrate dissolved in aqueous solution, because of the difficulty of evaporating the water from the solution prior to dissolution in DMF. Polarography in DMF, however, should prove to be a relatively rapid, precise and accurate method for the analysis of solid nitrate samples. The polarographic method of analysis is less complex and more rapid than most other methods of analysis for nitrate.[11–13] It is applicable to analysis of samples containing potassium nitrate, sodium nitrate, ammonium nitrate, calcium nitrate, and other DMF-soluble nitrate compounds. Since the nitrate wave occurs at a half-wave potential that is more negative than that for most other reductions, it should only rarely be necessary to perform a separation prior to the analysis.

As a check of the utility of polarography in DMF as a method of analysis for a "real" sample, the nitrate in a solid commercial fertilizer was dissolved in 0.1*M* TBAP in DMF and analysed polarographically by the standard addition technique. In this particular case the nitrate wave had a polarographic maximum of the first kind. The maximum did not interfere with the analysis since the diffusion current could be

measured at a potential (about −2.8 V) more negative than that for the maximum. Of four identical samples taken for the analysis, three yielded identical results. The average of the four results was 1.5% nitrate nitrogen as compared with the manufacturer's analysis, as listed on the package, of 1.2% nitrate nitrogen.

The difference between the two results could easily be attributable to sampling error since no special care was taken to ensure that the sample taken was representative of the several distinct types of particle found in the fertilizer. Although further testing of the polarographic method for determination of nitrate is warranted, it is clear that the method has several advantages and is applicable to at least some practical analyses.

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SYNTHESIS AND PROPERTIES OF A NEW CHELATING RESIN CONTAINING THE OXIME GROUP

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Summary—A macroreticular polystyrene-based chelating resin with oxime and diethylamino functional groups has been synthesized. The resin is stable in acid and alkaline solutions; no decrease in nitrogen content or capacity for sorption of copper(II) is observed when it is exposed to 3*M* hydrochloric acid and 1*M* sodium hydroxide for 7 days. The resin has higher selectivity for copper(II) than for other metal ions tested and the time required for 50% uptake of copper(II) is 15 min. The highest capacity for copper(II) is 2.0 mmole/g at pH 6.0. In a column operation, quantitative recovery of copper(II) is achieved by elution with 1*M* hydrochloric acid, and the resin can be used repeatedly.

Various oxime compounds, such as dimethylglyoxime, benzoinoxime, and salicylaldoxime are well known as highly selective reagents for the detection and/or determination of some heavy metal ions. Substituted 2-hydroxybenzophenone oximes, marketed by General Mills Inc. as extractants for copper(II) ion under the name of LIX reagents, have also been applied in hydrometallurgy[1] and extraction chromatography.[2,3]

Although some previously introduced chelating resins[4–7] containing oxime groups sorb metal ions such as copper and nickel through the oxime groups, they are not extensively used in practice. In view of the properties of oxime groups, however, further search for chelating resins containing the oxime group seems justified. Rapid equilibration[8] is regarded as an important factor in the practical usefulness of a chelating resin, as well as selectivity and sorption capacity. In the present study we synthesized a new macroreticular resin containing the oxime group together with the diethylamino group, which was introduced in an attempt to increase the hydrophilic nature and stability of the resin. The characteristics of this resin in the sorption of some metal ions were examined.

EXPERIMENTAL

Synthesis of resins

Resin II. To 50 g of macroreticular polystyrene–divinylbenzene copolymer (7.5% divinylbenzene, 35–100 mesh fraction, resin I[9]), 500 ml of carbon disulphide were added. After the mixture had been stirred for 1 hr, finely ground anhydrous aluminium chloride (129 g) was added in one portion. To the mixture, 83 g of chloroacetyl chloride were added dropwise at 30–40°, and the stirring was continued at 30–40° for 6 hr more. The mixture was then poured onto finely crushed ice to which 2 litres of 10% hydrochloric acid had been added and then the solid phase was filtered off and washed with acetone, methanol, 10% hydrochloric acid and water, successively, and dried. A pale yellow resin (*ca.* 72 g) was obtained.

Resin III. Resin II (30 g) was added to 200 ml of ethyl acetate and stirred for 1 hr at room temperature, then 43 ml of diethylamine were added and the mixture was heated at 50° for 6 hr with stirring. The solid phase was filtered off and washed with methanol, water, 1*M* sodium hydroxide, water and methanol, successively, and dried. A pale yellow resin (*ca.* 34 g) was obtained. (N, 4.2%; Cl ≈ 0).

Resin IV. Resin III (30 g) was added to a mixture of pyridine (180 ml), hydroxylamine hydrochloride (30 g) and dried ethanol (120 ml) and then the mixture was heated at 90° for 12 hr with stirring. The solid phase was filtered off and was washed with methanol, water and methanol, successively, and dried. A pale brown resin (*ca.* 30 g) was obtained. (N, 9.9%; Cl ≈ 0).

Stability of resin IV

Dry resin IV (0.5 g) was shaken with 30 ml of acid or alkaline solutions of various concentrations for 7 days, and then filtered and washed with water, 0.1*M* sodium hydroxide and water, successively. After drying, the nitrogen content and sorption capacity for copper(II) were determined.

Water regain

A sample of dry resin IV was immersed in water, left under reduced pressure for a while, then allowed to stand for 24 hr. The resin was centrifuged and weighed, dried at 100° and then weighed again. Water regain was calculated from the difference in weight.

Sorption of metal ions on resin IV

To a glass-stoppered test-tube containing 100 mg of dry resin, 9 ml of 0.25*M* hydrochloric acid–0.25*M* sodium acetate solutions (adjusted to pH 1–7) were added. When this mixture had equilibrated, 1 ml of 0.1*M* metal ion solution was added to the test-tube, then the mixture was shaken at room temperature. After being shaken for a definite time, the mixture was filtered through glass wool to separate the resin and the amount of the metal ion remaining in the filtrate was determined by chelatometric titration.

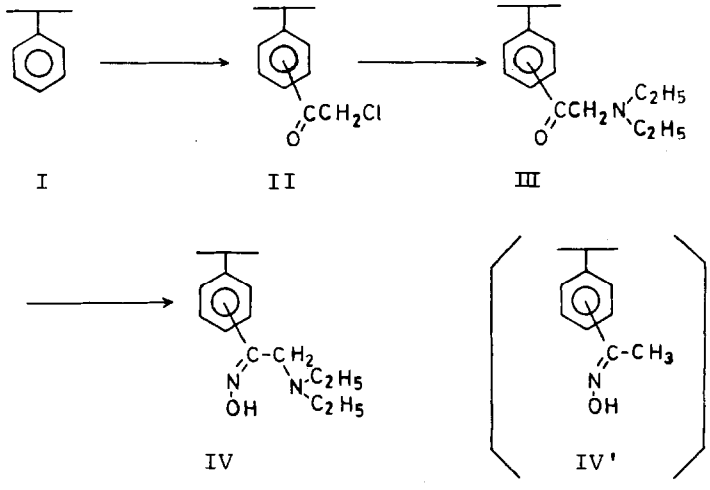
Recovery of copper(II) ion

Resin IV which had sorbed copper(II) (2.0 mmole/g) was shaken with hydrochloric acid or nitric acid for 2 hr. After filtration, the amount of copper(II) in the filtrate was determined by chelatometric titration. In column operation, 34 mg of copper(II) were loaded on a 0.7 × 17 cm column (resin IV, 2 g), and then copper(II) was eluted with 1*M* hydrochloric acid at a flow-rate of 2 or 4 ml/min.

RESULTS AND DISCUSSION

Synthesis and characterization of resin

The resin in this study was synthesized from 35–100 mesh styrene–divinylbenzene copolymer beads through the steps shown in Scheme 1.



Scheme 1.

In a preliminary experiment, we synthesized a resin IV', but this resin was unstable in acidic media and was not very hydrophilic. When shaken in 1*M* hydrochloric acid for 7 days, it lost 50% of its oxime groups.

We therefore planned the synthesis of resin IV which has both diethylamino and oxime groups, expecting this to increase the stability and hydrophilic nature of the resin. Figure 1 shows the infrared spectra of resins I–IV. Absorption bands at 1670 cm^{-1} ($\nu_{C=O}$) and 650 cm^{-1} (ν_{C-Cl}), which were observed for resin II, disappeared in the case of resin IV. In addition, resin IV showed an absorption band at 3400 cm^{-1}, based on the OH group. This spectral change corresponds to the reaction scheme presented above.

From the nitrogen content of resin IV, it was estimated that the functional groups were introduced onto about 60% of the aromatic rings of the resin.

The stability of resin IV in acid and alkaline solutions is shown in Table 1. The nitrogen content and the capacity for copper(II) decreased on treatment with 3*M* nitric acid, whereas no significant decrease was observed in the treatment with hydrochloric acid

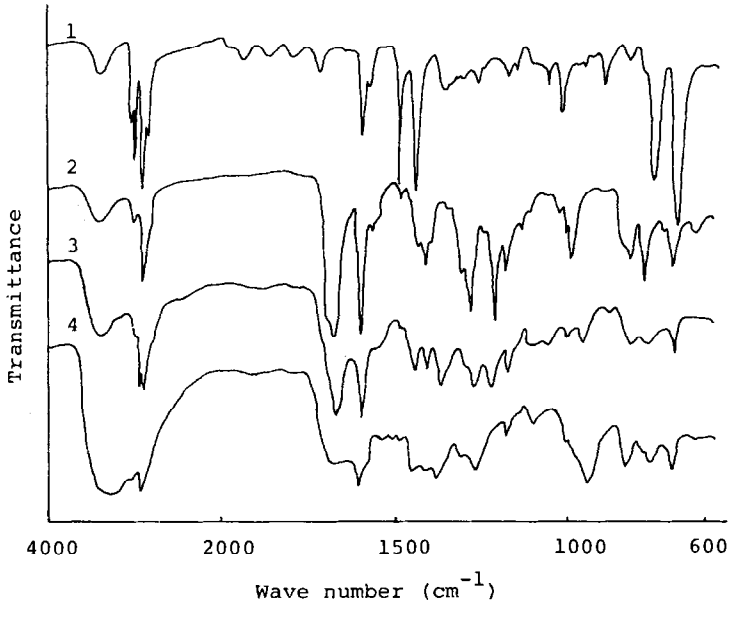


Fig. 1. Infrared spectra of resins (in KBr disks). 1, resin I; 2, resin II; 3, resin III; 4, resin IV.

Table 1. Stability of resin IV

Conditions			Capacity for Cu(II),
Reagents	Shaking time, *days*	*N*, %	*mmole/g*
0.1*M* HCl	7	9.9	2.0
1*M* HCl	7	9.6	2.0
3*M* HCl	1	9.6	2.0
	7	8.9	1.9
1*M* HNO_3	7	9.2	1.9
3*M* HNO_3	7	4.9	1.4
1*M* NaOH	7	9.9	2.0
none		9.9	2.0

and sodium hydroxide solution. Although the oxime group, in general, is not stable and readily hydrolysed by treatment with acid, it is fairly stable on this resin.

Sorption of metal ions

The high selectivity of resin IV toward copper(II) is illustrated in Fig. 2, which shows the sorption behaviour of eight metal ions at different pH on resin IV. The function of the oxime group is clearly indicated by comparison with a control experiment under the same conditions with Amberlite IRA-93, which has only the tertiary amino group as the functional group, and shows no significant sorption of copper(II). In addition, it is of interest that resin IV shows lower affinity for mercury(II). Generally, resins containing sulphur and nitrogen atoms as ligands have high affinity for both mercury(II) and copper(II).[9-11] Chelation of the type $-N-O-Me \leftarrow N(C_2H_5)_2-$ was assumed to occur, on the basis of the drop in pH observed when resin IV was shaken with the metal ion solutions.

The rate of sorption of copper(II) was determined by a batch operation. As shown in Fig. 3, the time required for 50% uptake of copper(II) from 0.03*M* copper(II) nitrate was 15 min. This fast equilibration rate may be related to the fairly high water regain (1.44 g/g). The capacity for copper(II) was about 2.0 mmole/g at pH 6. The presence of neutral salts such as sodium chloride and sodium nitrate (0.5*M*) did not affect the sorption of copper(II).

The break-through experiments were carried out by column technique. Copper(II) solution (0.032 mg/ml) was allowed to pass through a column loaded with 2 g of resin IV, at a flow-rate of 3 or 5 ml/min, and the amount of copper(II) in the collected effluent fractions was determined spectrophotometrically.[12] As shown in Fig. 4, the break-through curve for copper (II) shows that about 140 bed-volumes of feed solution can be passed through at a flow-rate of 3 ml/min without leakage of copper(II) into the effluent, and increase in the flow-rate causes a remarkable decrease in the efficiency of collection of copper(II).

Recovery of copper

Experiments on recovery of copper(II) from resin IV were carried out by batch operation, and the results shown in Table 2 indicate that copper(II) can be recovered with hydrochloric or nitric acid of concentration higher than 0.1*M*. In column operation, copper(II) was found to be completely eluted with less than 5 bed-volumes of 1*M* hydrochloric acid, and the elution curve was completely symmetrical. The results

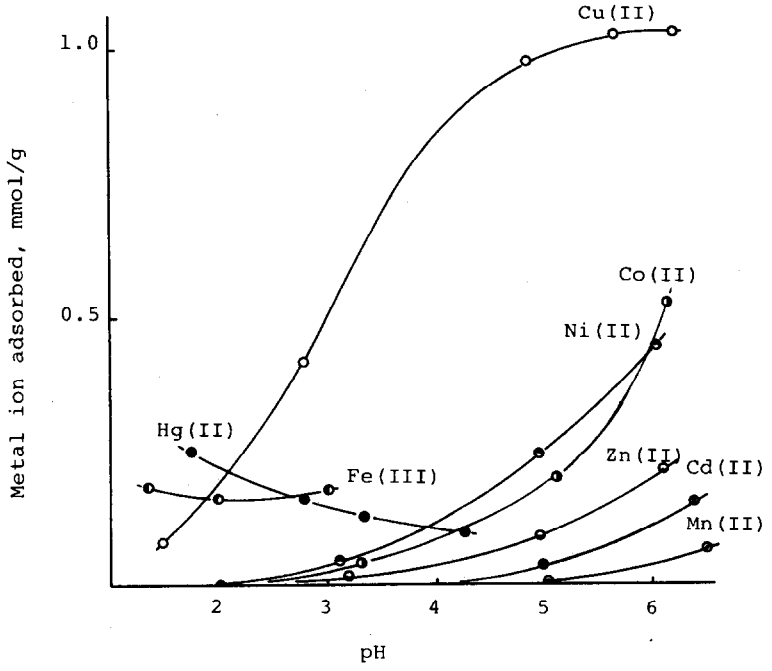


Fig. 2. Effect of pH on the sorption of metal ions. Shaking time 24 hr.

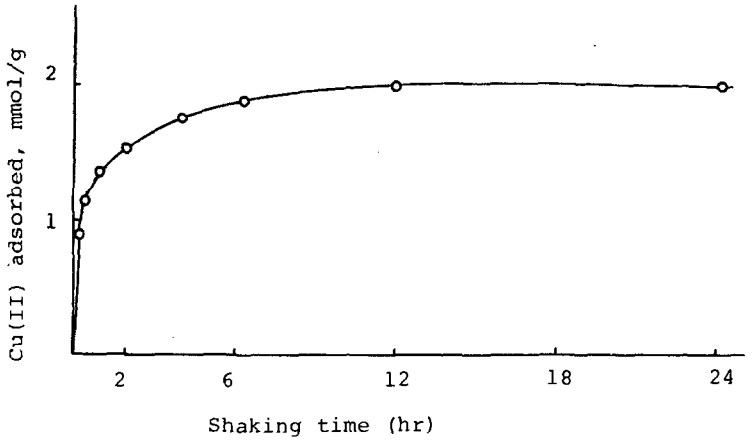


Fig. 3. Effect of shaking time on the sorption of Cu(II) at pH 6.0.

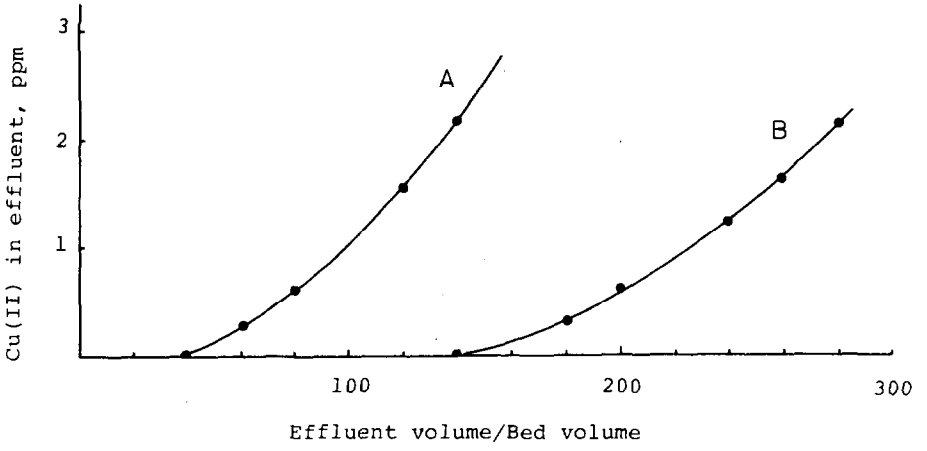


Fig. 4. Break-through curves for Cu(II). Column 1.0 × 9 cm; flow-rate (A) 5 ml/min, (B) 3 ml/min; feed 32 ppm Cu(II); pH 6.0.

Table 2. Recovery of Cu(II) by batch operation

Acid, *M*		Recovery, %
HCl	0.01	18
	0.1	93
	1.0	96
	3.0	100
HNO_3	0.01	15
	0.1	88
	1.0	96
	3.0	99

presented above suggest that resin IV can be applied to the concentration and separation of copper(II) effectively and repeatedly.

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ANODIC BEHAVIOUR OF A DROPPING LEAD AMALGAM ELECTRODE IN HALIDE MEDIUM IN THE PRESENCE OF EDTA

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Summary—The behaviour of the dropping lead amalgam electrode has been studied. Calculated and experimental current–voltage curves have been compared and an explanation has been given for the observed differences. Selective determination of metal ions appears to be possible in the presence of saturated chloride, 1*M* bromide and $10^{-2}M$ iodide by means of amperometric complex-formation titrations using normal pulse polarography with the dropping lead amalgam electrode.

In a previous paper,[1] amperometric complex-formation titrations of metal ions with end-point indication by means of a dropping bismuth amalgam electrode have been discussed. The bismuth amalgam electrode offers the advantage that the interference from halides in acid medium is much less than it is with dropping or rotating mercury electrodes (DME and RME).

It was felt that the use of other amalgams in place of mercury might further decrease the interference by chloride and bromide and might also make it possible to carry out titrations in iodide medium. According to the criteria which have been mentioned previously,[1] lead amalgam and cadmium amalgam would be worth considering: lead was preferred because it is somewhat less electronegative than cadmium.

It has been found that when a dropping lead amalgam electrode is used for end-point detection, the interference from chloride and bromide is almost completely eliminated, and even in iodide medium titrations appear to be possible.

THEORETICAL

Theoretical current–voltage relationships will be derived for the anodic dissolution of lead from a dropping lead amalgam electrode in the presence of (*i*) chloride, (*ii*) bromide, (*iii*) iodide and (*iv*) EDTA in order to investigate the applicability of this electrode in complexometric titrations. The derivations are similar to those for the dropping bismuth amalgam electrode.[1] It is assumed that all equilibria are established rapidly in all cases and that the Nernst equation is obeyed. The activities in the solution are considered to be equal to the concentrations. A comparison will be made with the experimental data.

(*i*) Chloride medium

If lead–chloride complexes are formed, the reaction at the electrode surface is:

$$Pb + nCl^- \rightleftharpoons PbCl_n^{2-n} + 2e^-$$

The current–voltage relationship can be given by:

$$E = E^0_{(Pb^{2+},Pb)} - \frac{0.059}{2}\log \alpha_{Pb(Cl)_{bulk}} + \frac{0.059}{2}\log\frac{i}{k_{Pb(Cl)_n}} - \frac{0.059}{2}\log\frac{i_d^{Pb} - i}{k_{Pb}} \qquad (1)$$

where k is the polarographic proportionality constant. The formation of insoluble $PbCl_2$ does not occur under the experimental conditions.

(*ii*) Bromide medium

In this case Cl has to be replaced by Br in equation (1).

(*iii*) Iodide medium

Two cases have to be taken into consideration: the formation of lead–iodide complexes, which leads to an equation similar to equation (1); the formation of insoluble lead iodide. In the latter case the current–voltage curve can be given by:

$$E = E^0_{(Pb^{2+},Pb)} + \frac{0.059}{2}\log K_{s0}^{PbI_2} - \frac{0.059}{2}\log[I^-]^2 - \frac{0.059}{2}\log\frac{i_d^{Pb} - i}{k_{Pb}} \qquad (2)$$

(*iv*) The equation for the potential of the electrode in the case of lead-EDTA complex-formation is given by:

$$E = E^0_{(Pb^{2+},Pb)} - \frac{0.059}{2}\log K_{Pb\text{-}EDTA} + \frac{0.059}{2}\log \alpha_{EDTA(H)} + \frac{0.059}{2}\log\frac{i}{i_d^{EDTA} - i} - \frac{0.059}{2}\log\frac{i_d^{Pb} - i}{k_{Pb}} \qquad (3)$$

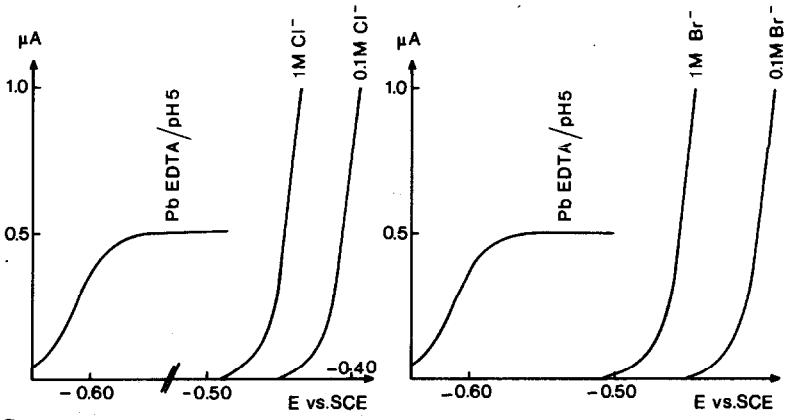

Fig. 1. Current–voltage curves for (a) chloride media and (b) bromide media calculated according to equations (1) and (3).

Equation (3) is independent of the side-reactions of lead(II) with chloride, bromide, iodide and hydroxide ions*.

The following constants taken from the literature have been used in calculating the current–voltage curves; $E^0_{(Pb^{2+},Pb)} = -0.367$ V *vs.* SCE,[2] $\log K^{PbI_2}_{s0} = -8.01$,[3] $\log K_{PbEDTA} = 18.0$.[4] For $Pb^{2+} + n Cl^- \rightleftharpoons PnCl_n^{2-n}$, $\log\beta_1 = 0.90$; $\log\beta_2 = 1.36$; $\log\beta_3 = 1.45$;[3] For $Pb^{2+} + n Br^- \rightleftharpoons PbBr_n^{2-n}$, $\log\beta_1 = 1.11$; $\log\beta_2 = 1.43$; $\log\beta_3 = 2.18$;[3] For $Pb^{2+} + n I^- \rightleftharpoons PbI_n^{2-n}$, $\log\beta_1 = 1.26$; $\log\beta_2 = 2.80$; $\log\beta_3 = 3.42$; $\log\beta_4 = 3.92$.[3] At pH 5 $\log\alpha_{EDTA(H)}$ is 6.6.[4] The remaining values have been determined experimentally: $i_d^{Pb} = 6$ μA for $1.24 \times 10^{-3}M$ lead in the amalgam, hence $k_{Pb} = 5 \times 10^3$ μA.l.mole^{-1}; $i_d^{EDTA} = 0.5$ μA for $10^{-4}M$ EDTA, hence $k_{EDTA} = 5 \times 10^3$ μA.l.mole^{-1}. It is supposed that k_{Pbx_n} has the same value as k_{EDTA}.

Figure 1 shows some current–voltage curves for chloride medium (Fig. 1a) and bromide medium (Fig. 1b), calculated on the basis of equations (1) and (3).

Figure 2 gives some current–voltage curves calculated for iodide by means of equations (1), (2) and (3). In the absence of EDTA the formation of PbI_n^{2-n} complexes predominates at lower iodide concentrations whereas at higher concentrations the insoluble PbI_2 is formed.

EXPERIMENTAL

The amalgam for the dropping amalgam electrode was prepared by dissolving metallic lead in mercury. The metallic lead was rinsed with acetone and distilled water and kept in $1M$ perchloric acid[5] in order to remove lead oxides. Even after 1 hr no hydrogen evolution was observed, which might be explained by overvoltage of hydrogen on lead.[6] After heating, hydrogen was evolved, indicating that the lead oxides had been removed. After being rinsed with distilled water and dried, a known amount of lead was dissolved in a known amount of mercury under nitrogen. The concentration of lead in the amalgam was $1.24 \times 10^{-3}M$. The amalgam was stored under nitrogen.

The apparatus, including the titration cell, was the same as that used for the studies of bismuth amalgam but with the coulometer and the platinum electrode left out. All experiments were performed with a PAR model 174 polarographic analyser in the normal pulse mode if not stated otherwise. All potentials were referred to the SCE. During the measurements of the current–voltage curves, the ionic strength was kept constant; a value of 4.5 μA was observed for the limiting anodic current for the lead and this was used in calculating the theoretical curves.

Reagents and procedure were the same as given before.[1]

RESULTS AND DISCUSSION

Figure 3 shows a comparison of the experimental current–voltage curves with the theoretical ones calculated from equation (1) for chloride (Fig. 3a), bromide (Fig. 3b) and according to equations (1) and/or (2) for iodide (Fig. 3c). There is fairly good agreement between the theoretical and the experimental curves in the case of chloride and bromide, but the agreement is somewhat poorer for $0.01M$ and $0.1M$ iodide. Also from Fig. 3 it can be seen that the experimental curves occur at more negative potentials than the cal-

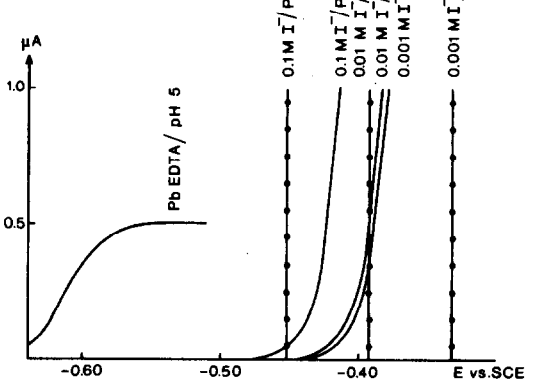

Fig. 2. Current–voltage curves for iodide media calculated according to equations (1), (2) and (3).

* This was incorrectly represented in equation (9) in our previous paper.[1] This implies that the two BiEDTA waves in Fig. 2 of that paper are to be located at a half-wave potential of −0.35 V and the three BiEDTA waves in Fig. 3 at a half-wave potential of −0.21 V.

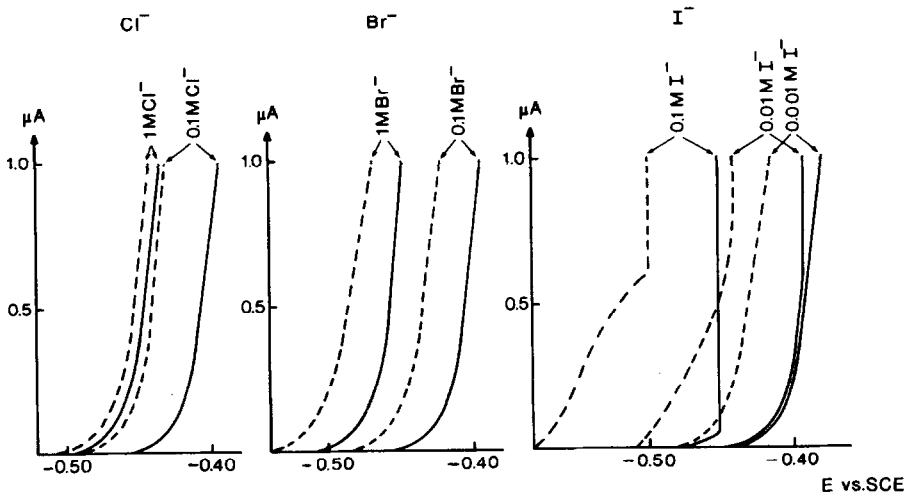

Fig. 3. Current–voltage curves for (a) chloride media and (b) bromide media calculated according to equation (1), and (c) for iodide media calculated according to equations (1) and (2) (——). Corresponding experimental current–voltage curves (---).

culated ones, whereas in the case of the bismuth amalgam electrode the experimental curves occur at more positive potentials than the theoretical ones.

In order to explain this difference, literature values of the stability constants for the lead–halide complexes have been compared. The values for the bromide and iodide complexes given by Bond and Hefter,[7] determined at a DME, are larger than those commonly quoted in the literature. The authors attribute this difference to adsorption of lead–halide complexes on the mercury. In our case we used the lead amalgam electrode in halide medium, for which the conditions are different. We therefore decided to study adsorption of halide ions on the lead amalgam electrode and the consequences of adsorption on the anodic oxidation of the lead from the amalgam. To detect any difference between adsorption of halide ions at a DME and at a dropping lead amalgam electrode, several electrocapillary curves were determined in different media. A downward shift on the positive side of the electrocapillary curve, which leads to a shift of the potential value of the maximum, forms an indication of a specific adsorption. The capillary curves in Fig. 4a,b were determined with different capillaries. Therefore a small difference in the height of the curves could be observed. However, the maxima occur at the same potential, indicating that there seems to be no difference in the adsorption of halide ions on mercury and on lead amalgam. A difference can be seen on the positive side of the maximum of the curve, which can be attributed to the oxidation of lead. These lead(II) ions will react with the halide ions. This process might influence the slope of the electrocapillary curve.

Sluyters-Rehbach *et al.*[8,9] have studied the influence of adsorption of electroactive species on the half-wave potential as well as on the slope of the reversible d.c. polarogram. A similar treatment can be given for the dropping lead amalgam electrode. Consider the following reversible electrode reaction:

$$Pb(Hg) + nX^- \rightleftharpoons PbX_n^{2-n} + 2e^-$$

where X is a halide ion.

As we are mainly interested in concentrations of halide much larger than the concentration of lead in the amalgam, it is supposed that $\bar{c}_X = c_X^*$, where $\bar{c}$ = surface concentration and c^* = bulk concentration; $c^*_{PbX_n} = 0$.

Then

$$\alpha_{Pb(X)} = 1 + \beta_1 c_X^* + \beta_2 c_X^{*2} + \beta_3 c_X^{*3} \qquad (4)$$

From $\alpha_{Pb(X)}$ and $E^0 = -0.367$ V ($Pb^{2+} + 2e^- \rightleftharpoons Pb$) it is possible to calculate the conditional potential E' ($PbX_n^{2-n} + 2e^- \rightleftharpoons Pb + nX^-$). For a steady state at the electrode surface the current can be given by:

$$i = nFA \frac{D_{Pb}}{\bar{c}_{Pb}} (c^*_{Pb} - \bar{c}_{Pb})$$

$$= nFA \frac{D_{PbX_n}}{\bar{c}_{PbX_n}} \bar{c}_{PbX_n} + nF\Gamma_{PbX_n} dA/dt \qquad (5)$$

in which Γ_{PbX_n} = moles of PbX_n adsorbed per unit of surface area.

It is supposed that Γ_{PbX_n} does not depend on time. The thickness of the diffusion layer for the different species will be given by $\bar{c}_i = (\frac{1}{7}\pi t D_i)^{1/2}$, where D is the diffusion coefficient.

For incomplete electrode coverage it is useful to express Γ_{PbX_n} as

$$\Gamma_{PbX_n} = \theta \Gamma^{max}_{PbX_n} (\theta = \text{degree of electrode coverage}) \qquad (6)$$

From equations (5), (6) and the Nernst equation, it follows that:

$$E = E' - \frac{0.059}{2} \log \frac{i_d - i}{i - nF\theta\Gamma^{max}_{PbX_n}(dA/dt)}. \qquad (7)$$

From this equation it can be seen that the half-wave potential shifts towards negative potentials. The term

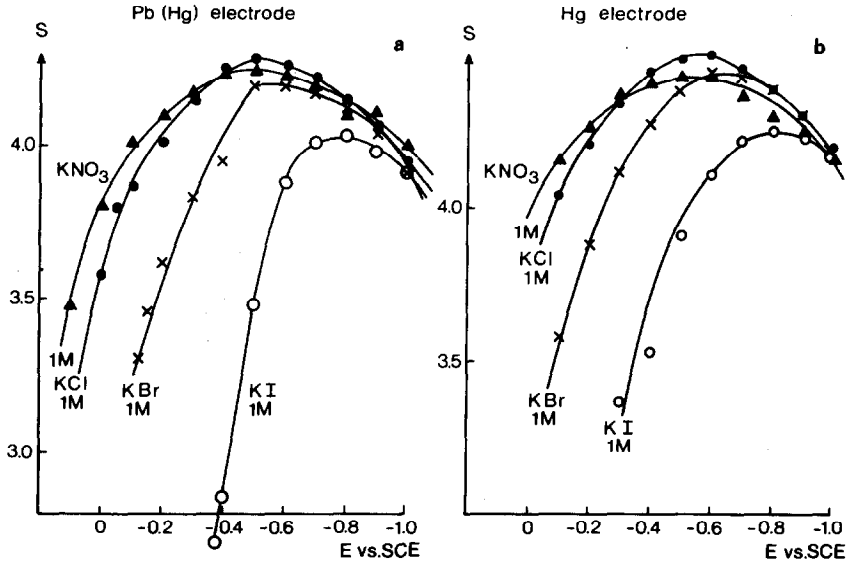

Fig. 4. Electrocapillary curves at (a) a dropping lead amalgam electrode, both in different media and (b) a DME.

$nF\theta\Gamma^{max}_{PbX_n}\, dA/dt$ in equation (7) causes a deviation from linearity in the plot of log i_d–i/i *vs.* E.

In order to check this effect, anodic-sampled d.c. polarograms with the dropping lead amalgam electrode (drop-time 2 sec) in chloride, bromide and iodide media were recorded. For chloride solutions (10^{-3}–$4M$) the logarithmic plots were linear and the slope was about 30 mV in nearly all cases. The plots for bromide and iodide solutions are slightly curved (Fig. 5a,b) from which it can be concluded that adsorption increases with increasing halide ion concentration and that the extent of adsorption is larger for iodide than for bromide. At iodide concentrations larger than $5 \times 10^{-3}M$ a peak appears on the steep part of the current-sampled d.c. polarogram near the half-wave potential and therefore also in the logarithmic curve (Fig. 5b). Information about this peak was obtained by recording current–time curves with a slowly dropping lead amalgam electrode (drop-time about 8 sec) at fixed potentials. The resulting curves indicate that strong adsorption takes place at the peak potential.

In conclusion it can be said that the shift of the experimental curves to negative potentials as compared with the theoretical ones is caused by strong adsorption of lead ions formed by oxidation from the lead amalgam electrode in the presence of bromide and iodide.

Titrations

In order to investigate the applicability of the lead amalgam electrode as an end-point detector in amperometric complex-formation titrations, current-sampled d.c. polarograms with a dropping lead amalgam

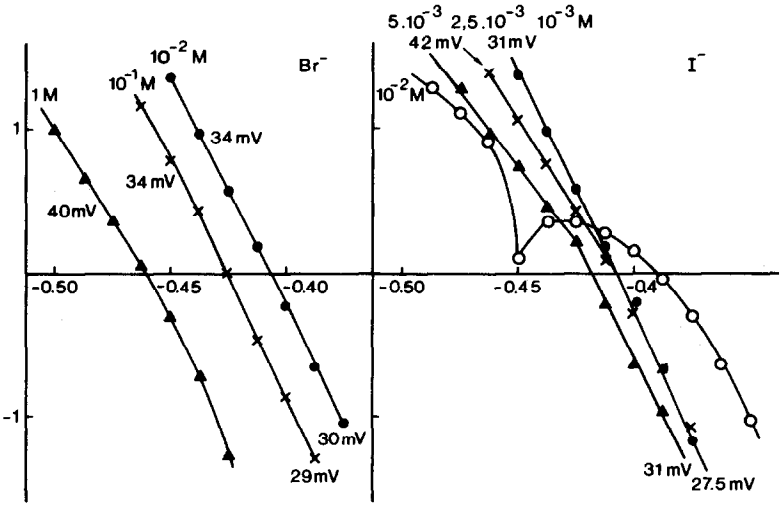

Fig. 5. A plot of $\log(i_d\text{-}i)/i$ *vs.* E in (a) bromide media and (b) iodide media. The $0.1M$ bromide curve has been shifted 12.5 mV in the negative direction for representational clarity.

Table 1. Determinations of metal ions in the presence of halide ions in 0.07*M* acetate buffer at pH 4.8

Titrant	Procedure*	Indicator electrode potential, *E vs.* SCE, *V*	Conc. of other ions	Species titrated, *μg*/10 *ml* taken		found	Error, %	Relative std.devn., % (no. of detns.)	
EDTA	D	−0.50	0.6*M* KCl	9.82	Zn(II)	10.1	+2.9	4.1	(4)
EDTA	D	−0.50	1*M* KCl	9.82	Zn(II)	10.2	+3.9	6.0	(4)
EDTA	D	−0.51	1*M* KCl	4.91	Zn(II)	4.79	−2.4	6.3	(4)
EDTA	D	−0.52	0.5*M* KBr"S"	9.82	Zn(II)	9.75	−0.7	3.1	(4)
EDTA	D	−0.54	1*M* KBr"S"	9.82	Zn(II)	9.71	−1.1	5.9	(4)
EDTA	D	−0.48	$10^{-3}M$ KI	9.82	Zn(II)	9.69	−1.3	1.0	(4)
EDTA	D	−0.50	$10^{-2}M$ KI	9.82	Zn(II)	9.78	−0.4	1.8	(4)
EDTA	D	−0.54	1*M* KBr"S"	6.70	VO^{2+}	6.83	+1.9	4.4	(4)
EDTA	D	−0.50	1*M* KCl	5.00	VO^{2+}	5.00	—	6.7	(4)
Th(IV)	B	−0.52	4*M* NaCl"S"	7.00	Ga(III)	5.89	−15.9	4.7	(4)
Th(IV)	B	−0.49	$5.10^{-3}M$ KI	7.00	Ga(III)	6.99	−0.1	1.9	(4)
Th(IV)	B	−0.53	4*M* NaCl"S"	3.50	Ga(III)	2.93	−16.3	4.5	(3)

* D = direct titration; B = back-titration.
† "S" means Suprapure

Table 2. Critical values for halide ions at pH 5 in the anodic amperometric complex-formation titrations with EDTA

	Rotating mercury electrode	Dropping bismuth amalgam electrode	Dropping lead amalgam electrode
Cl^-	$10^{-3}M$	$5 \times 10^{-2} - 10^{-1}M$	~4*M* (saturated)
Br^-	$10^{-5}M$	$10^{-2}M$	1*M*
I^-	impossible	impossible	$10^{-2}M$
ref.	(10)	(1)	this work

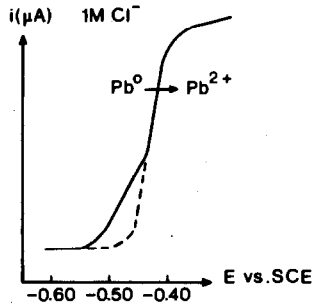

Fig. 6. Current-sampled d.c. polarogram in 1*M* KCl/pH-5 acetate buffer in the presence (——) and absence (---) of EDTA.

electrode in acetate medium at pH 5 were recorded in the presence and absence of EDTA in solutions containing halide ions. Figure 6 shows such a polarogram in 1*M* chloride medium. A linear relationship was obtained between the height of the anodic ligand wave and the concentration of the ligand as long as the ratio of the concentration of the free ligand to the concentration of lead in the amalgam did not exceed a value of about 0.7. Care was taken not to exceed this value during the present investigation.

Despite the precautions taken to avoid spontaneous oxidation of the lead in the amalgam, the concentration of lead did decrease slowly. After a long period of time a thin black film was observed on the surface of the amalgam in the reservoir. This film is a mixture of mercury oxide and lead oxide, caused by oxidation by traces of oxygen.

The applicability of the lead amalgam electrode in halide ion medium is summarized in Table 1. The applicability is restricted to metal ions that have a half-wave potential more negative than that of lead or are electroinactive in that potential range. Otherwise cathodic waves can interfere with the anodic wave used for indication of the end-point.

Titrations in the $10^{-5}M$ range have to be carried out at pH values not much lower than 5 because of the value of the stability constant of the PbEDTA chelate. Therefore the determination of such elements as Ga(III) has to be performed by means of a back-tritration to avoid hydrolysis. In this case EDTA is added in excess to the solution of the metal ion at low pH, after which the pH is adjusted with the buffer solution to pH 4.8.

The limit of determination, compared with that with the bismuth amalgam electrode, seems to be affected unfavourably by the strong adsorption of halides at the lead amalgam electrode.

Table 2 shows a survey of the interferences by halide ions at pH 5 for anodic amperometric complex-formation titrations at the rotating mercury electrode, the dropping bismuth amalgam electrode and lead amalgam electrode. The interferences from halide ions decrease markedly in this order.

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THE EXTRACTION OF NOBLE METALS WITH n-OCTYLANILINE

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Summary—The extraction of noble metals with n-octylaniline at varying concentrations of different mineral acids was studied, and optimum conditions for their separation from the base metals commonly present in platinum-bearing materials were established. The successful application of the procedure to the analysis of mattes, sludges, and flotation concentrates is shown. The lower limit of determination in such materials is 100 ppm for Pt and Ir, 40 ppm for Ru, and 10 ppm for Pd and Rh.

The separation of Pt, Pd, Ir, Rh, and Ru as a group from Cu, Ni, Fe, and Co by extraction with n-octylaniline from 3*M* hydrochloric acid has been described by Vasilyeva *et al.*[1] After their extraction, the noble metals are determined by atomic-absorption spectrophotometry (AAS) either in the organic phase or, after destruction of the extractant and fusion with sodium peroxide, in aqueous solution in the presence of lanthanum as releasing agent. Variations in sensitivity led the Russian authors to propose the determination of some of the elements in the organic phase and of others in aqueous solution.

Because the determination of small amounts of noble metals in materials containing large amounts of base metals is difficult, it was decided in the present work to evaluate the effectiveness of n-octylaniline as an extractant for the noble metals from a variety of platinum-bearing materials and process solutions. Special emphasis was placed on aspects of the extraction not covered by the Russian authors, namely the preparation of n-octylaniline, the amounts of aqueous and organic phase used, and the determination of distribution coefficients for base metals other than Cu, Co, Ni, Fe, and Zn. In addition, the extraction of the noble metals into n-octylaniline from mineral acids other than hydrochloric acid was investigated with a view to possible back-extraction of these metals from the organic phase so that the noble-metal mixtures could be analysed by AAS in aqueous solution.

EXPERIMENTAL

Apparatus

Varian Techtron models AA5 and AA6 atomic-absorption spectrophotometers and Varian Techtron hollow-cathode lamps were used.

Reagents

The noble metals, in the form of sponge or wire and having a certified purity of 99.95%, were obtained from Engelhard Industries, or Johnson Matthey Ltd. The preparation of standard solutions of Au, Pt, and Pd has been described elsewhere.[2] Rh, Ru, and Ir solutions were prepared by dissolution of the metals in sealed tubes by chlorination.[3]

Vasilyeva *et al.* gave no description of how the reagent was prepared, and, since it was not commercially available, n-octylaniline was initially prepared in this laboratory from octylbenzene by a procedure analogous to that for the preparation of aniline.[4] However, because of the difficulties encountered with emulsion formation, n-octylaniline was subsequently prepared from n-octanol and aniline in the presence of zinc chloride at an elevated temperature.[5]

Preparation of n-octylaniline

The method of preparation of n-octylaniline would appear to have some significance in the behaviour of this reagent when used for noble metal separations, particularly with respect to the formation of emulsions, which prevent quantitative separation of the organic phase. The preparation based on reaction of benzene chloride with caprylic acid in the presence of ammonia to give an ammonium carbonyl which is then reduced by zinc metal in hydrochloric acid medium to a reduction product which is then extracted with methylene chloride from alkaline medium, gives a product, obtained after distillation under vacuum, which is also prone to form emulsions. This product is essentially a *para*-substituted compound with only traces of the *ortho*-compound present.

The n-octanol (210 g), aniline (433 g) and anhydrous zinc chloride (317 g) were placed in a reaction vessel fitted with a reflex condenser, a thermometer, and a Dean and Stark water-separating device. An inert atmosphere was maintained by passage of nitrogen over the reaction mixture during heating at a temperature of 255° for 21 h. The reaction mixture was then cooled and treated with dilute sulphuric acid (120 g/l.). The vessel containing the slurry was placed in crushed ice, and ammonia was added until the solution was neutral. The yellow oil formed was separated by means of a separating funnel, and the aqueous phase was extracted once with ether to increase the yield of octylaniline. The oil and the ether extract were combined, and sodium hydroxide pellets were added to remove emulsified water. The mixture was then decanted and the ether evaporated. A yield of more than 70% of the theoretical yield of n-octylaniline was obtained. If desired, the n-octylaniline was purified by distillation under vacuum (0.08 mmHg) at a temperature of 101°. The distilled product had a refractive index of $n_{25}^{D} = 1.5160$.

The resulting product had a b.p. of 302° and an f.p. of

11°, and the formation of emulsions was minimal. Depending on the impurities present, the colour of the reagent varied from light yellow to yellow-red. Purification of the reagent by vacuum distillation showed no advantage with respect to the extraction of the noble metals, and the organic phase had a tendency to solidify after extraction, depending on the room temperature. This was not observed in the presence of small amounts of impurities. However, n-octylaniline is soluble in most solvents; unless otherwise stated, di-isobutyl ketone (DIBK) was used as the diluent.

Extraction of noble metals

Process solutions containing the noble metals require adjustment of the hydrochloric acid concentration to 3*M*.

Solid samples were fused with sodium peroxide fusion and the cooled melts were leached with hydrochloric acid. The solutions were evaporated to moist dryness, and the residues treated with concentrated hydrochloric acid. If present in large amounts, silica was removed by dehydration and filtration, and the solution was again evaporated. The residue was dissolved in 3*M* hydrochloric acid, and the noble metals were extracted with a 1*M* solution of n-octylaniline (aqueous/organic phase ratio = 5) by shaking for 10 min. The extraction was repeated with fresh n-octylaniline solution, and the organic phases were combined. The organic solution was diluted with 5 times its volume of DIBK and mixed. The noble metals were back-extracted with two 5-ml portions of 7*M* perchloric acid, being shaken for 10 min for each extraction. The aqueous perchloric acid phases were combined, uranium solution (1%) was added as releasing agent, and the noble metals were measured against a similar set of standard solutions by flame AAS. The instrumental parameters are given in Table 1.

Most of the investigational work was done with the air–acetylene flame and a Techtron 10-cm grooved burner. Maximum sensitivity for platinum, palladium and gold was observed when a lean flame was used. Rhodium required a normal flame, and ruthenium a rich flame.

RESULTS AND DISCUSSION

In agreement with the results obtained by Vasilyeva *et al.*,[1] it was found that when 10-ml portions of 3*M* hydrochloric acid containing all the noble metals were shaken with 2-ml portions of 1*M* n-octylaniline in DIBK, Ru, Pt, Ir and Au were quantitatively extracted in 10–15 min. Rh and Pd, although more than 90% extracted in 10 min, require 2 hr shaking for practically quantitative removal. With aqueous/organic phase ratios from 1 to 20, Ru, Pt, Ir, and Au were extracted quantitatively. The extraction of Rh decreased slightly at a phase ratio greater than 1, but then remained constant. The extraction of Pd, however, decreased rapidly when the phase ratio was greater than 5.

Effect of the concentration of n-octylaniline

Vasilyeva *et al.* used 2*M* n-octylaniline solution for the extraction of the noble metals,[1] but this was found to be rather viscous and therefore inconvenient to handle. Concentrations of n-octylaniline in DIBK from 0.1 to 2*M* gave quantitative extraction of Au, Ir, Pt, and Ru, and the maximum extraction of Pd (92%) was obtained at an n-octylaniline concentration $\geq 1M$. The extraction of Rh (90%) increased slightly with increasing concentration of the reagent but did not become quantitative even at a concentration of 2*M* n-octylaniline. It was therefore decided that 1*M* solutions of n-octylaniline and an aqueous/organic phase ratio of 5 should be used in all the experimental work, and that two extraction stages with a shaking time of 10 min each should be adopted.[4] This gave quantitative extraction of Pt, Ir, Ru and Au, and almost complete extraction of Rh. Vasilyeva *et al.*, using a phase ratio of 10, obtained satisfactory extraction only for Ir, Pt and Rh.

Effect of concentration of different mineral acids

The effect of sulphuric, hydrochloric, nitric, and perchloric acid of varying concentrations on the extraction of the noble metals was investigated. The mixed noble metals in their chloride form were dissolved in the acids, and 10-ml portions were shaken for 10 min with 2-ml portions of 1*M* n-octylaniline in DIBK. After the phases had separated, the concentration of the noble metals in the aqueous phase was determined. The results are shown in Figs. 1–4.

From sulphuric acid medium Pd and Au were well extracted over the total range tested, the extraction of Pt, Ru, and Ir decreased with increasing acid concentration, and Rh was poorly extracted over the whole range.

From hydrochloric acid Pt, Ir, and Au were extracted quantitatively over the whole concentration range tested, Ru was extracted quantitatively at acid concentrations from 2 to 9*M*, and the extraction of Pd decreased rapidly with increasing hydrochloric acid concentration, whereas that of Rh increased slightly up to an acidity of 8*M* and then slowly decreased. In agreement with Vasilyeva *et al.*,[1] a hydrochloric acid concentration of 3*M* was chosen for the extraction of all the noble metals, which represents a comprise between the concentration giving the maximum extraction of Pd and that giving the maximum extraction of Rh.

Table 1. Instrumental parameters for the Techtron AAS Spectrophotometer

Parameter	Pt	Pd	Rh	Ru	Au
Wavelength, *nm**	265.9	244.8	343.5	349.9	242.8
Spectral band-width, *nm*	0.17	0.17	0.17	0.33	0.33
Lamp current, *mA*	10	7	5	10	4
Flow-rate, *l./min*	1.75	1.75	2.25	3	1.75

* The most sensitive lines were used.

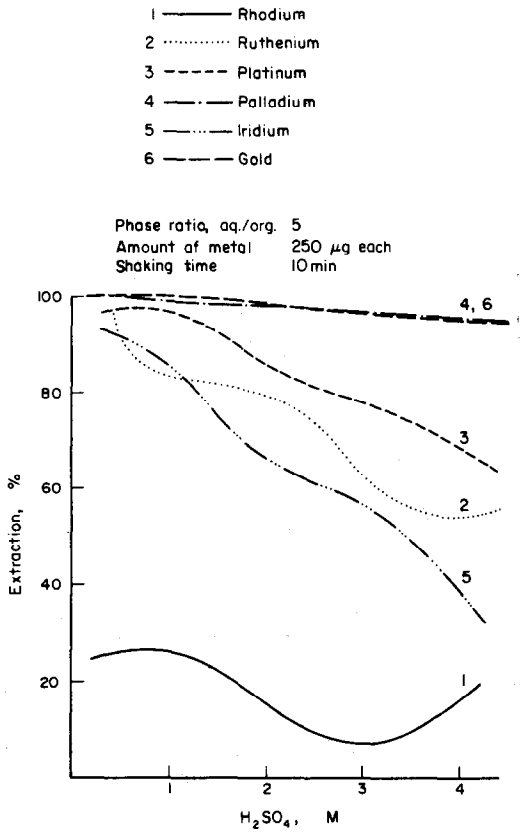

Fig. 1. Effect of hydrochloric acid concentration.

From nitric acid Pd and Au were well extracted over the whole range. The extraction of Pt and Ir decreased with increasing nitric acid concentration, whilst the extraction of Rh and Ru remained low over the whole concentration range tested.

All the platinum-group metals showed decreasing extraction with increasing concentrations of perchloric acid and were not extracted at all at perchloric acid concentrations greater than 7*M*. Au was well extracted over the whole concentration range tested, with a slight decrease at acid concentrations greater than 6*M*.

Back-extraction and determination of the noble metals

From the extraction data for the different mineral acid media it was clear that, with the exception of Au, all the noble metals could be stripped with perchloric acid at concentrations greater than 7*M*.

It was found experimentally that the back-extraction was quantitative when the organic phase containing the noble metals was diluted five times with DIBK. Initially, a single 10 ml portion of 7*M* perchloric acid was used, but because of the solubility of this medium in DIBK leading to low recoveries of the aqueous phase, two extractions with 5 ml of 7*M* acid and a shaking time of 10 minutes were used to increase the recovery of the precious metals from the organic phase. Uranium was added as releasing agent, combined to the aqueous phases, and the solution was diluted to volume with water for measurement of the noble metals by AAS.

That DIBK was the most suitable of the diluents tested is shown in Table 2. Chloroform, benzene and petroleum ether gave quantitative extraction, but stripping was impaired because of the formation of precipitates in either the organic or the aqueous phase (Table 2).

Behaviour of Os

Because of the insensitivity of Os in AAS measurement, its determination in the presence of the other noble metals was not attempted. However, its behaviour under the extraction conditions was of interest and was investigated accordingly. It was found that hexachloro-osmate was quantitatively extracted from

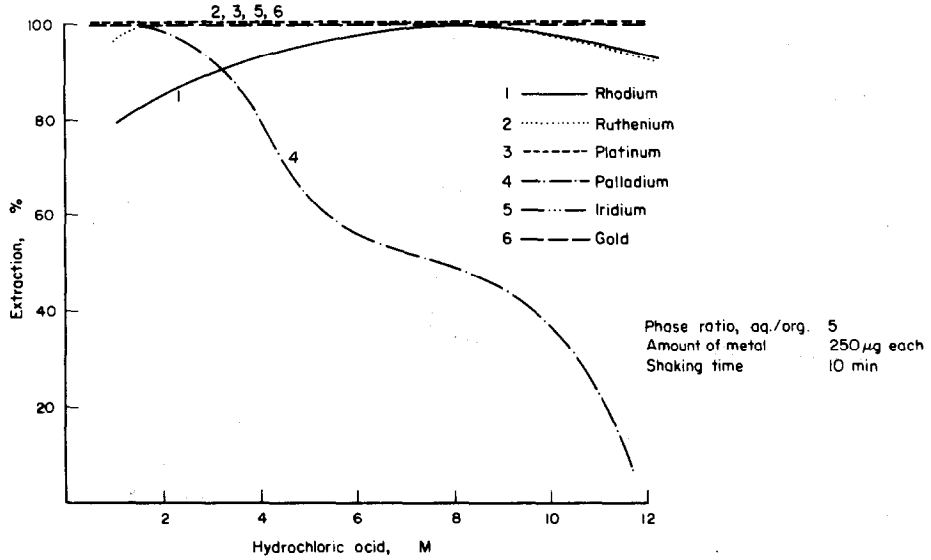

Fig. 2. Effect of nitric acid concentration.

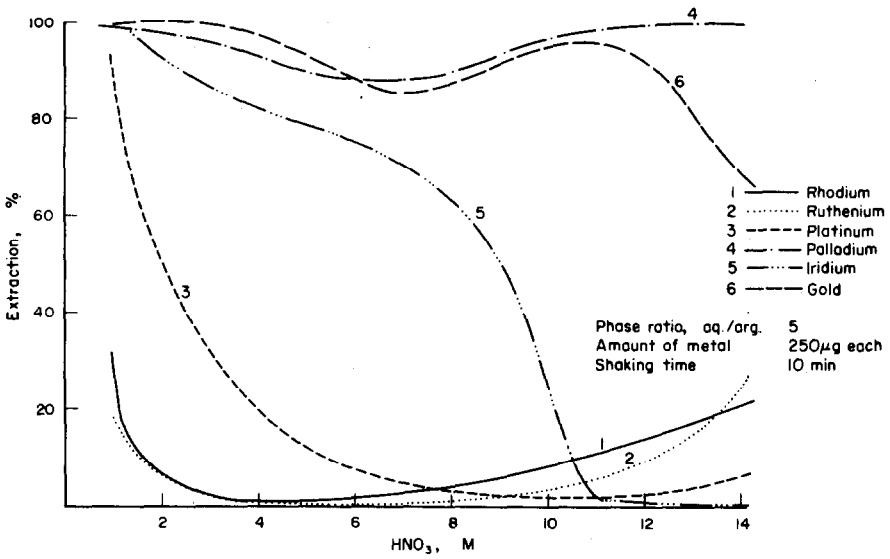

Fig. 3. Effect of sulphuric acid concentration.

3*M* hydrochloric acid and back-extracted with 7*M* perchloric acid. Os was determined colorimetrically with thiourea[7] after the solution had been sufficiently diluted for the perchloric acid not to interfere.

Capacity of n-octylaniline

The capacity of n-octylaniline for the individual noble metals was determined by shaking 10-ml portions of 3*M* hydrochloric acid containing the individual noble metals (100 mg each) with 2 ml of 1*M* n-octylaniline in DIBK for 10 min. The maximum amounts extracted were 24 mg of Rh, 38 mg of Ru, 86 mg of Pt, 60 mg of Pd, 86 mg of Ir, and 98 mg of Au.

Effect of base metals

Initially, chloroform was used as the diluent in the examination of extraction of the base metals. When it was replaced by DIBK for the extraction of the noble metals, the extraction of the base metals was re-examined. The results obtained are compared in Table 3. The extraction of Ni, Cu, Co, and Cr was not affected by the change of diluent. Pb and As showed slightly increased extraction with DIBK, and Zn, Sb, Se, Te, Bi, Sn, and Fe were extracted to a considerably larger extent. However, when the noble metals were back-extracted with 7*M* perchloric acid, only Zn and Bi were also back-extracted and Sn to the extent of 20%. As, Sb, Se, Te, Pb, and Fe were only 3, 0.5, 0, 2, 4, and 1.6% back-extracted respectively, and at these levels would not interfere in the AAS determination of the noble metals. The back-extraction of Zn, Bi, and Sn is not serious, because of the very low levels at which these metals occur in platinum-bearing materials.

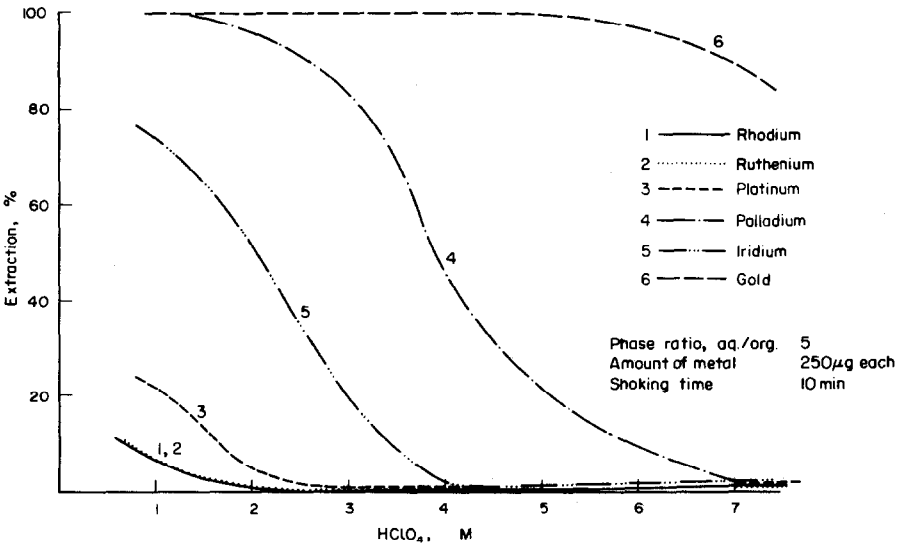

Fig. 4. Effect of perchloric acid concentration.

Table 2. Effect of different diluents on the back-extraction of noble metals (amount of metal: 250 μg; volume of diluent: ≃ 20 ml each)

Diluent	Re-extraction, % Rh	Ru	Pt	Pd	Ir	Au	Observations
DIBK	100	100	100	100	100	0	Both phases clear
Chloroform	7	16	29	54	32	—	Precipitate in aqueous phase
Benzene	87	80	100	59	89	44	Precipitate in organic phase
Petroleum ether	79	63	100	78	81	63	Precipitate in organic phase

The pattern of extraction of base metals when using 2*M* n-octylaniline in toluene is similar to that obtained with the 1*M* reagent in DIBK except for Te for which no co-extraction was observed, and Fe for which the co-extraction was intermediate between that with DIBK and that with chloroform (Table 3).

Extraction of Rh

Although Rh was extracted quantitatively from synthetically prepared solutions, it was not extracted from 3*M* hydrochloric acid after a solid sample had been fused with sodium peroxide. Extractable Rh chloro-complexes were obtained only after evaporation of the sample solution and repeated treatment of the residue with concentrated hydrochloric acid as described in the procedure.

Absorption spectra of Rh species

In order to show that the Rh complexes initially present after peroxide fusion were indeed different from the extractable form obtained after treatment with concentrated hydrochloric acid, absorption spectra of the respective species were recorded. All the solutions contained equal amounts of Rh, and were diluted ten times for measurement in the ultraviolet region of the spectrum.

An aliquot of a standard solution of Rh was evaporated in an alumina crucible, and the residue was fused with sodium peroxide. The melt was leached with 3*M* hydrochloric acid and, after the liquor had been boiled and cooled, the spectrum was recorded against a reference solution prepared in the same way but not containing Rh. The spectrum obtained (Fig. 5, Curve A) shows only indistinct shoulders in the visible region of the spectrum but a distinct peak in the ultraviolet region at 225 nm ($\epsilon = 1.7 \times 10^4$ l. mole^{-1}.cm^{-1}). After evaporation of the solution and repeated treatment of the residue with concentrated hydrochloric acid followed by dissolution in 3*M* hydrochloric acid, an absorption spectrum (Fig. 6, Curve A) with maxima at 510 nm ($\epsilon = 196$), 400 nm ($\epsilon = 190$), 250 nm ($\epsilon = 1.7 \times 10^4$) and 215 nm ($\epsilon = 1.7 \times 10^4$) was obtained, which, according to the spectra obtained by Blasius and Preetz[8] and Wolsey *et al.*,[9] indicated that a mixture of the anionic species $[RhCl_5(H_2O)]^{2-}$ and $[RhCl_6]^{3-}$ was present. The absorption spectrum of the standard Rh solution in 20% hydrochloric acid (prepared as described previously[3]) that was used in this study (Fig. 5, Curve B), with maxima at 505, 400 and 214 nm ($\epsilon = 1.8 \times 10^4$) clearly indicated the presence of $[RhCl_5(H_2O)]^{2-}$ as the predominant species. The complex $[RhCl_6]^{3-}$ could be shown to be present only when an aliquot of the standard solution was boiled for a prolonged time with concentrated hydrochloric acid (Fig. 5, Curve C). The maxima at 515 nm ($\epsilon = 206$), 410 nm ($\epsilon = 175$), 252 nm ($\epsilon = 2 \times 10^4$) and 212 nm ($\epsilon = 1.6 \times 10^4$) correspond satisfactorily to those obtained by Wolsey *et al.*[9] for a freshly prepared solution of Na_3RhCl_6 and by Blasius and Preetz[8] when an Rh solution had been boiled for several hours in 7*M* hydrochloric acid.

Table 3. Effect of different diluents on the extraction of base metals (10 mg of each metal, phase ratio aq/org = 5, shaking time 10 min)

Metal	Extraction, % 1*M* n-octylaniline in DIBK	1*M* n-octylaniline in chloroform	2*M* n-octylaniline in toluene
Zn	39	13	38
Sb	85	45	84
Se	28	10	18
Te	53	—	—
Pb	68	60	—
As	4	—	—
Ni	—	—	—
Cu	—	—	—
Co	—	—	—
Cr	10	10	—
Bi	87	75	95
Fe	50	—	20
Sn	60	16	50

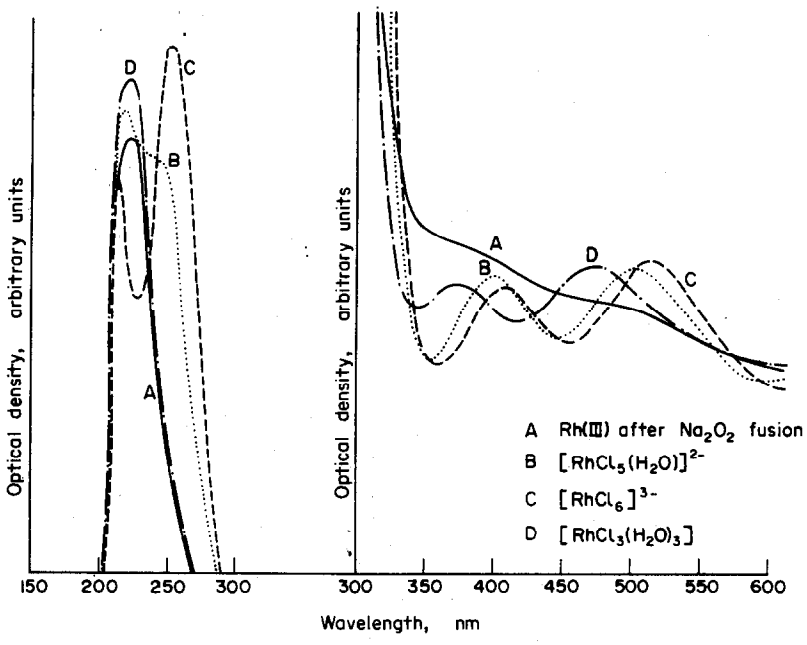

Fig. 5. Absorption spectra of rhodium(III) complexes.

To show further the displacement of the absorption maxima towards increasingly shorter wavelength, the absorption spectrum of an Rh solution in 1*M* hydrochloric acid, which had been standing for approximately six weeks, was recorded. As shown in Fig. 5, Curve D, absorption maxima were obtained at 475 nm ($\epsilon = 206$), 375 nm ($\epsilon = 180$) and 225 nm ($\epsilon = 1.9 \times 10^4$) indicating[8] the presence of the neutral species $RhCl_3(H_2O)_3$ as an essential constituent of the solution.

Since the absorption spectrum obtained for an Rh solution after peroxide fusion did not correspond to any of the spectra obtained for the hydrolysis complexes of Rh as shown in this investigation and elsewhere,[8,9] the formation of hydroxy-aquo complexes was tentatively assumed. To substantiate this reasoning, sodium hydroxide was added to a standard Rh solution in hydrochloric acid until it became strongly alkaline, and the absorption spectrum was measured (Fig. 6, Curve B). A single peak was obtained at 420 nm ($\epsilon = 227$) and a small peak at 207 nm. After the solution had been acidified with hydrochloric acid, the peak in the visible region disappeared and the peak at 207 nm increased slightly (Fig. 6, Curve C). When

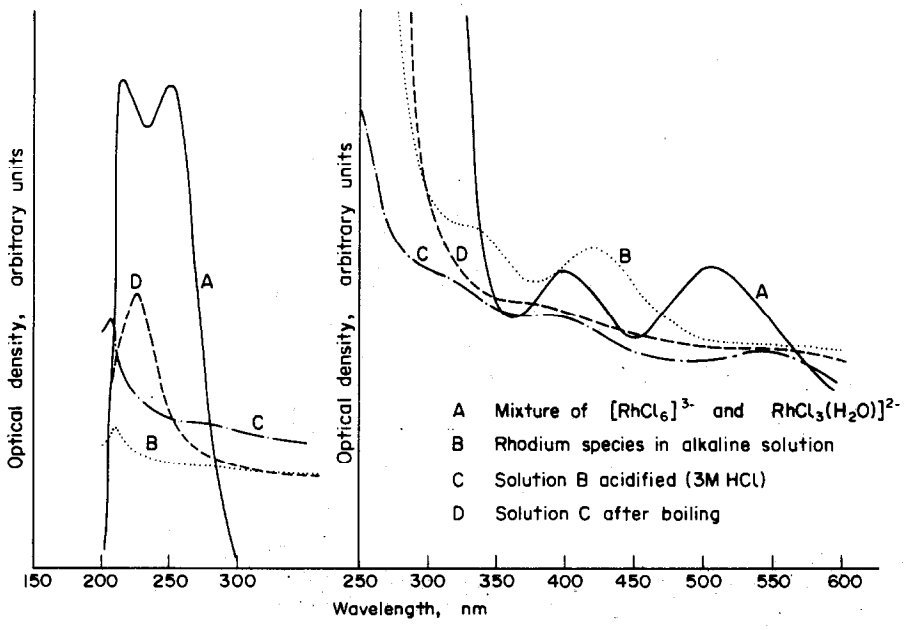

Fig. 6. Absorption spectra of rhodium(III) complexes.

Table 4. Analysis of reference samples.

Element	Metal content %							
	Pt–Pd Sludge 21/72		Matte leach residue 25/73		Matte leach residue 26/73		Flotation concentrate 9/72	
	Proposed method	Independent method	Proposed method	Independent method	Proposed method	Independent method	Proposed method	Independent method
Platinum	4.36 (±0.1)*	4.28 (±0.2)	4.4 (±0.02)	4.8	2.07 (±0.01)	2.2	731 (±7)	700
Palladium	2.89 (±0.1)	3.09 (±0.1)	1.96 (±0.02)	2.25	0.89 (±0.01)	1.02	244 (±4)	292
Rhodium	0.12 (±0.01)	0.15 (±0.01)	0.22 (±0.01)	0.25	0.09 (±0.01)	0.09	43 (±1)	41
Ruthenium	0.07 (±0.01)	0.08 (±0.01)	0.36 (±0.01)	0.42	0.23 (±0.01)	0.26	85 (±2)	85
Iridium	0.05 (±0.01)	0.06 (±0.01)	ppm 792 (±100)	ppm $709_{(\pm 76}^{101})$	ppm 251 (±1)	ppm 270	~11	~12

* The figures in brackets give the range of values in %.

Phase ratio, aq/org: 5, shaking time: 2 × 10 min., aqueous phase: 3*M* HCl, back extraction: 2 × 5 ml 7*M* $HClO_4$.

the acidified solution (approximately 3*M* hydrochloric acid) was boiled, the indistinct peak at 207 nm shifted towards 225 nm ($\epsilon = 5.8 \times 10^3$) and the spectrum obtained (Fig. 6, Curve D) resembled that obtained after peroxide fusion. The shift of the peak towards a longer wavelength with an increase in absorption was assumed to be indicative of the substitution of aquo or hydroxy groups by chloride ions and, therefore, the formation of hydroxy–aquo–chloride complexes of the type $[Rh(H_2O)_4(OH)Cl]^+$ and/or $Rh(H_2O)_3(OH)Cl$. Further confirmation of the presence of such species by techniques such as ion-exchange was outside the scope of this investigation.

Application of the method to platinum-bearing materials

The proposed procedure was applied to a variety of samples of widely varying noble-metal content (Table 4), and the results obtained were compared with those obtained after a cation-exchange or a fire-assay procedure. Although a slight negative bias was apparent in all cases for Pd, the average results obtained for the other metals were considered satisfactory. Approximately one hour is needed for the extraction and back-extraction of the noble metals, and sixteen samples can be handled simultaneously if an automatic shaker is used.

CONCLUSIONS AND RECOMMENDATIONS

The investigations reported in this work basically confirm the findings of Vasilyeva *et al.* that n-octylaniline is a useful group extractant for the noble metals. The reagent has been prepared in a form that has acceptable characteristics, and conditions for the extraction of the noble metals have been examined in more detail.

The determination of the platinum metals in aqueous medium after back-extraction leads to a much simpler procedure. The use of a lower concentration of extractant, besides conserving reagent, appears to enable a higher ratio of sample to reagent solution to be used, which can be of advantage when dealing with trace amounts of noble metals, as in refinery process streams.

On the other hand, a shorter analysis time, in addition to improved sensitivity and therefore limits of determination, can be achieved if the noble metals are determined directly in the organic phase by flame AAS. In that case, however, chloroform is recommended as the diluent for the n-octylaniline because of the reduced interference from co-extracted base metals. The chloroform present would have to be removed either by evaporation or a further dilution with a more suitable diluent (*e.g.* a ketone) for interference-free measurement by AAS. Alternative methods such as thin-film X-ray fluorescence, neutron-activition, or flameless AAS could equally be applicable to the analysis of the extract.

From the distribution data for the noble metals in mineral acids, it can be seen that the separation factors are large enough to facilitate the separation of the noble metals not only from base metals but also from each other if n-octylaniline is used as the stationary phase in reverse-phase extraction chromatography in columns. The feasibility of such an approach will be tested in this laboratory and the results reported in a later communication.

A comparison of the merits of n-octylaniline with those of an extractant such as *S*-(1-decyl)-*N,N'*-diphenylisothiouronium bromide (DDTU)[10] showed that the extraction of the noble metals from synthetic solutions in hydrochloric acid is of the same order. The time needed for equilibration is shorter for n-octylaniline, namely 10 as compared with 90 min for DDTU. Further, the noble metals, with the exception of Au, can be back-extracted from n-octylaniline but not from DDTU.

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ELECTROTHERMAL ATOMIC-ABSORPTION SPECTROMETRY OF ANTIMONY BY USE OF A MOLYBDENUM MICRO-TUBE ATOMIZER

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Summary—Electrothermal atomization of antimony has been investigated to clarify the atomization characteristics and interferences from diverse elements, for accurate determination of traces of antimony. Thiourea served to lower the atomization temperature of antimony and to improve the sensitivity. Germanium and phosphoric acid were found to have a pronounced effect on atomization of antimony. The interference of various elements was suppressed in the presence of thiourea. A method involving extraction for determining antimony in metallurgical and geological samples is described.

Atomic-absorption spectrometry with a carbon rod or a graphite furnace atomizer has been used for determination of antimony.[1–3] However, the carbon atomizer causes interference by carbide formation and the loss of metal atoms by diffusion through the walls of the carbon tube. Attempts have been made to cover the inner surface of the carbon tube with tantalum foil to preclude these effects. Goleb and Midkif[4] preferred the tantalum-strip atomizer for the determination of antimony. In flameless atomic-absorption spectrometry, it is important for the atomizer to reach a sufficiently high temperature before an appreciable fraction of the element disappears out of the light path by diffusion. Moreover, a fast-response detection system is necessary to record a rapidly occurring atomization without distortion.

In the present work, we investigated the electrothermal atomization of antimony with a metal atomizer and a fast-response detection system to clarify the atomization characteristics and interference phenomena and to develop a favourable atomization technique for the determination of antimony in metallurgical and geological samples.

EXPERIMENTAL

Apparatus

Atomic-absorption measurements were made with a Nippon Jarrell-Ash 0.5-m Ebert-type monochromator coupled to an R106 photomultiplier tube (Hamamatsu TV Co.) and JEOL AA-HMA signal-control unit as a signal-amplifier. The output signal from the signal-control unit was displayed on an Iwatsu MS-5021 Memoriscope.

The atomizer was a molybdenum micro-tube (25 mm long and 1.5 mm bore)[5] mounted in the absorption chamber (300 ml volume) which was purged with argon at a flow-rate of 0.48 ml/min and hydrogen at a flow-rate of 0.02 ml/min. The tube temperature was measured as previously described.[6]

The light-source was an antimony hollow-cathode lamp (Hamamatsu TV Co.). The analytical wavelength used was 217.6 nm. Background absorption was compensated. All sample solutions were injected with a glass micropipette.

Reagents

Stock solution of antimony(III) was prepared by dissolving antimony(III) potassium tartrate in water. Antimony(V) solution was prepared from potassium antimonate. These solutions were used as the basis of dilute solutions, which were freshly prepared immediately before use. All reagents were of analytical-reagent grade.

Determination of antimony in metallurgical and geological samples

Metallurgical samples. Decompose 0.2 g of sample (1–10 ppm Sb) with *aqua regia* and evaporate the solution to dryness on a water-bath. Dissolve the residue in 1.0 ml of 5% tartaric acid solution and 9.0 ml of conc. hydrochloric acid. Transfer 2.0 ml of the solution to a separatory funnel, add 0.5 ml of sodium nitrite solution (5%) and shake to oxidize to antimony (V), let stand for 20 min, add 0.5 ml of 5% urea solution to decompose excess of nitrite, then extract the antimony by shaking for 5 min with 3.0 ml of methyl isobutyl ketone. Take an aliquot of the organic phase and mix it with an equal volume of 2% thiourea solution in alcohol. Place 1 μl of this mixture in the micro-tube atomizer and atomize the antimony. If the iron content is high shake the organic extract with 2*M* hydrochloric acid to minimize the amount of iron present. Compensate for background absorption by use of a deuterium lamp, by measurement on a separate aliquot.

Prepare a calibration curve by extracting antimony from standard solutions as above.

Rock samples. Decompose 1 g of sample with 4 ml of conc. nitric acid and 4 ml of conc. hydrofluoric acid in a "Uni-Seal" decomposition vessel by heating at 120° in an electric oven for 3 hr. After the decomposition, transfer the solution to a Teflon beaker and evaporate to dryness on a water-bath. Repeat the evaporation after addition of 5 ml of conc. hydrochloric acid. Dissolve the residue in hydrochloric acid and proceed as for metallurgical samples.

RESULTS AND DISCUSSION

Atomization characteristics of antimony

Antimony was atomized from both antimonite and antimonate to find the atomization characteristics of antimony. The antimony solutions were dehydrated at 100° and the residues ashed at 200°. Then antimony was atomized by heating to a final temperature

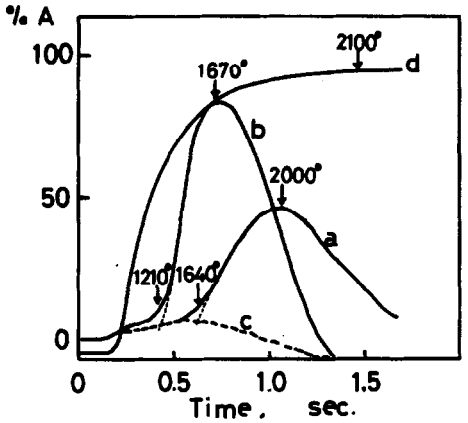

Fig. 1. Memoriscope traces for atomization of antimony: *a*, Sb 0.5 ng; *b*, Sb 0.5 ng and thiourea 4 μg; *c*, background (tube heated without sample); *d*, temperature increase.

of 2100°. Memoriscope traces showed somewhat similar absorption profiles for both antimonite and antimonate. It is known that antimony pentoxide forms the trioxide on heating, which may account for the similarity. The pronounced effect of thiourea on atomization of antimony is shown in Fig. 1. The atomization temperature of antimony was lowered in the presence of thiourea, and an increase in sensitivity resulted. Antimony is co-ordinated by the sulphur atom in thiourea, and sulphide may be formed from this complex in an ashing step. The most likely path to formation of gaseous antimony atoms in the molybdenum micro-tube atomizer may involve direct thermal dissociation of the compound. Because antimony has a fairly high vapour pressure (100 mmHg at 1280°), this mechanism of atom-formation appears to be feasible. Aggett *et al.*[9] also considered that direct thermal dissociation was responsible for atom-formation in metal-based atomizers. Therefore, the atomization behaviour of antimony would be influenced by the thermal stability of the compound used. Antimony sulphide has a lower heat of formation than the oxide ($-\Delta H_f^0$ = 42 and 169 kcal/mole for the sulphide and trioxide, respectively). This may be the reason for the lower atomization temperature of antimony in the presence of thiourea. The effectiveness of addition of a sulphur-containing complexing agent in atomization was also observed for arsenic[5] and bismuth.[6] The effect of thiourea was much more remarkable for antimony than for arsenic. The atomization characteristics of antimony from antimonite were also similar to those for antimonate in the presence of thiourea. The same phenomena were observed with thioacetamide in place of thiourea.

The addition of thiourea improved the absorption profile of antimony to give a higher peak absorption and a narrower width. The improvement in sensitivity was about 87%.

Effect of hydrogen flow-rate

Hydrogen was mixed with the argon purge gas to protect the micro-tube atomizer from oxidation. However, the signal for antimony became smaller with increasing hydrogen flow-rate. Therefore, a very low flow-rate of hydrogen is recommended.

Interferences

The possible interference of various elements was examined. The elements tested include arsenic, bismuth, copper, gallium, germanium, iron, lead, magnesium, nickel, selenium and silver. Arsenic and selenium were added as arsenite and selenious acid, respectively. Germanium solution was prepared from germanium dioxide dissolved in dilute sodium hydroxide. Other elements were added as their nitrates. All the samples were checked for background effects and absorption due to the heated micro-tube and interferents. Absorptions were traced on the Memoriscope for atomization of antimony in the presence of 100-fold amounts of various elements (Fig. 2). A marked shift of maximum absorption temperature for antimony was not observed in the presence of arsenic, bismuth, copper, iron, lead, nickel and silver although the signal for antimony was enhanced or depressed.

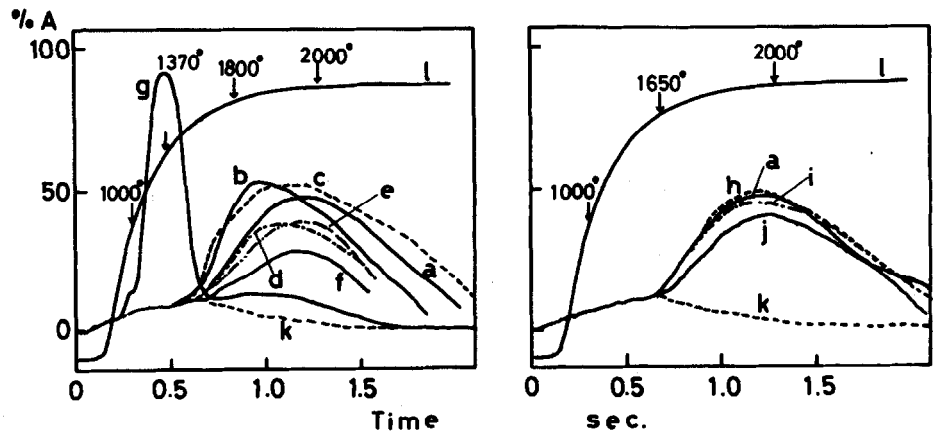

Fig. 2. Memoriscope traces for interference by 50 ng of various elements in determination of 0.5 ng of antimony: *a*, Sb alone; *b*, Sb and Se; *c*, Sb and Mg; *d*, Sb and Ga; *e*, Sb and Pb; *f*, Sb and Ag; *g*, Sb and Ge; *h*, Sb and Bi; *i*, Sb and Cu; *j*, Sb and Ni; *k*, background; *l*, temperature increase.

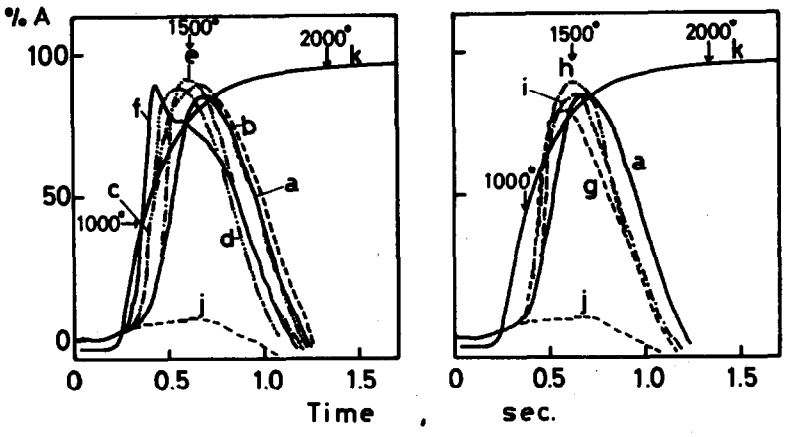

Fig. 3. Memoriscope traces for interference by 50 ng various elements in the presence of thiourea (antimony 0.5 ng): *a*, Sb alone; *b*, Sb and Se; *c*, Sb and Ga; *d*, Sb and Pb; *e*, Sb and Ag; *f*, Sb and Ge; *g*, Sb and Bi; *h*, Sb and Cu; *i*, Sb; *j*, background; *k*, temperature increase.

A remarkable depression of the antimony signal resulted from the presence of lead and silver. Gallium, germanium, magnesium and selenium lowered the temperature at which the antimony signal was maximal. A peculiar effect was observed for germanium. In this case, antimony was atomized at very much lower temperature. The origin of this effect was difficult to elucidate.

Figure 3 demonstrates the effects of diverse elements on atomization of antimony in the presence of thiourea. Antimony was atomized at lower temperature irrespective of the other elements present, but the temperature at which the antimony signal was maximal shifted from that for pure antimony. The peak absorptions were the same within 2.6% when various other elements were present.

Acids gave striking interference in atomization of antimony even at concentrations of 0.01*M*. Figure 4 shows the Memoriscope traces for antimony in the presence of hydrochloric, nitric, perchloric, phosphoric and sulphuric acids. Small absorption peaks were observed at about 1210°. Their origin is not evident, but molecular absorption was observed only for phosphoric acid. The atomization temperature of antimony was lowered in the presence of phosphoric acid, possibly because phosphoric acid is reactive toward most metals and oxides at elevated temperature. Perchloric acid caused marked suppression of antimony absorption. The first absorption peaks were increased in atomization of antimony from 0.1*M* nitric or perchloric acid. No evidence of molecular absorption was found for these absorption peaks. Therefore, the cause of these absorption peaks was difficult to elucidate. Only single absorption peaks were shown in atomization of antimony from 0.1*M* solutions of other acids, but molecular absorption was observed at about 1450° for phosphoric acid. Similar atomization profiles were recorded in the presence of phosphoric and hydrochloric acids when thiourea was present.

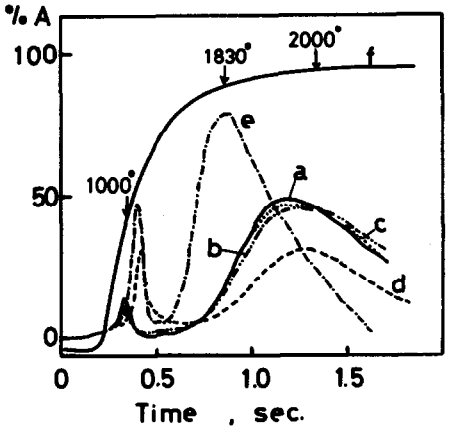

Fig. 4. Memoriscope traces for interference of acids in antimony absorption: *a*, 0.01*M* HCl; *b*, 0.01*M* HNO_3; *c*, 0.01*M* H_2SO_4; *d*, 0.01*M* $HClO_4$; *e*, 0.01*M* H_3PO_4; *f*, temperature increase.

Measurements combined with extraction

Because various elements and acids produce many interference effects in the atomization of antimony, the antimony must be isolated from interferents for its accurate determination. Solvent extraction is preferred for this purpose. Antimony(V) can be extracted effectively into methyl isobutyl ketone from hydrochloric acid medium. The Memoriscope trace for antimony atomized from the extracted species resembled that for aqueous solution and addition of thiourea also gave the same effect as in aqueous solution. Iron(III) is extracted along with antimony(V), and in large amounts interferes in the atomization of antimony. However, the interference is suppressed by stripping the iron(III) with 2*M* hydrochloric acid.

The effect of other extracted species on the antimony signal can be suppressed by mixing an alcoholic solution of thiourea with the extracts.

The results obtained by the proposed methods are shown in Table 1. No measurable signal was found for antimony without the addition of thiourea, for

Table 1. Determination of antimony in metallurgical and geological samples

Sample	Antimony, *ppm* Found*	Reported
Tin metal	9.5	9.6‡
Copper metal	4.1	4.9‡
Lead metal†	0.88	0.93‡
Aluminium metal§	100	100‡
Crude copper§	700	640‡
Rock AGV-1	4.3	4.5¶
Rock GSP-1	2.1	3.1¶
Rock PCC-1	0.92	1.4¶
Rock JB-1	0.21	0.22#
Rock JG-1	0.20	<0.6#

* Mean of three determinations.
‡ Values from other laboratories.
† Nitric acid was used for decomposition.
§ After decomposition of 0.1 g of sample the resultant solution was diluted to 25 ml with water and 5 ml of this solution were taken for analysis.
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determination of 4 ng of antimony in the presence of 4 μg of copper. The preliminary separation was also necessary for the determination of antimony with carbon atomizers. The molybdenum micro-tube atomizer needs only a short heating to provide an environment with uniform temperature throughout the atomizer and forms the maximum atom cloud concentration in an extremely short period of time, in contrast to conventional carbon atomizers. Therefore, a fast-response detection system is needed. With this atomizing device, the effective lifetime of the free atoms is longer than when a filament atomizer is used.

The atomization device is easy to make and gives more than 100 measurements without memory effects provided no acids in higher concentration are used. Acids in higher concentration shorten the life of the atomizer.

In flame atomic-absorption spectrometry, it is recommended that the standards are matched with respect to the matrix and the reagents used to prepare the samples but this is unnecessary for the determination of traces of antimony with the flameless atomizer.

Conclusions

Atomization of antimony is favoured by the addition of thiourea to the antimony solution and the sensitivity is also improved. Preliminary extraction of antimony is recommended for various samples because of the interferences of various elements and acids.

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ANION-EXCHANGE BEHAVIOUR AND SEPARATION OF METAL IONS ON DEAE-CELLULOSE IN OXALIC ACID MEDIA

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Summary—The anion-exchange behaviour of 30 metal ions on a weakly basic ion-exchanger (DEAE-cellulose) has been investigated in aqueous oxalic acid media over the concentration range 0.0010–0.50*M*. There are marked differences in adsorbability between ter- and quadrivalent metal and bivalent metal groups; the system offers good prospects for group separations. The adsorptions are moderate, generally a few orders of magnitude lower than those on Dowex 1 (a strongly basic resin). Procedures for the separations Se(IV)–Se(VI); As(III)–As(V); multicomponent separations Mn(II)–Co(II)–Cu(II)–Ti(IV)–Zr(IV) and Cd(II)–Zn(II)–Cu(II), are given to demonstrate the versatility of the system.

Oxalic acid is an attractive complexing agent for the anion-exchange chromatography of metals. Ter- and quadrivalent species such as Al(III), Fe(III), Ti(IV), Zr(IV) and Sn(IV) are known to form very stable oxalato complexes, having stabilities several orders of magnitude higher than those of many bivalent metal oxalate complexes. Ion-exchange in oxalic acid or oxalic acid–mineral acid media therefore offers an excellent means of separating bivalent and multivalent elements.[1,2] The early systematic study on anion-exchange in pure oxalic acid media was initiated by De Corte *et al.*,[3] who determined distribution coefficients of 12 elements on Dowex 1 X-8 resin. Nozaki and co-workers[4] have presented the distribution coefficients of 13 elements on Amberlite IR-120 in 0.1*M* oxalate as a function of pH (1.5–4.5) as well as the elution profile curves for 19 elements in 0.02 and 0.1*M* oxalate media over the pH range 2–4. Similarly, cation- and anion-exchange distribution coefficients of several elements in oxalic acid and potassium oxalate solutions, together with those in other carboxylic acid media, have been reported by Qureshi and others.[5] Extensive lists of anion-exchange distribution coefficients on AG 1 X-8 have been provided by Strelow *et al.*[1] for 36 elements in oxalic acid–hydrochloric acid mixtures. The versatility of the hydrochloric acid–oxalic acid system was demonstrated by the sequential elution of multicomponent mixtures. Distribution coefficient data for oxalic acid–nitric acid media are also available.[2] R_f values for 46 elements on a DEAE-cellulose layer in oxalic acid and oxalic acid–hydrochloric acid mixtures have been measured by Kuroda *et al.*[6] In the present work it was found that, in contrast to anion-exchange with DEAE-cellulose in aqueous mineral acid media,[7–9] a number of metals (particularly multivalent metals) are adsorbed on DEAE-cellulose from pure oxalic acid solution, sufficiently strongly to allow many column separations to be conducted.

EXPERIMENTAL

DEAE-cellulose (Brown Co., Berlin, N.H.) in the chloride form (0.91 meq/g) was treated with 0.01*M* sodium hydroxide and then converted into the oxalate form. This was stored in a vacuum desiccator containing phosphorus pentoxide. The distribution coefficients (K_d) defined by

$$K_d = \frac{\text{amount of metal in DEAE-cellulose phase/g of DEAE-cellulose}}{\text{amount of metal in solution phase/ml of solution}}$$

were measured at 25° as described in a previous paper.[10] The equilibration period was 6 hr for mixtures containing 0.5 g of DEAE-cellulose, 4 μmole of metal ion and 40.0 ml of oxalic acid solution of various concentrations (0.0010, 0.010, 0.030, 0.10, 0.30 and 0.50*M*). The metal ions were determined by appropriate instrumental methods such as spectrophotometry, polarography or atomic-absorption spectrophotometry.

RESULTS AND DISCUSSION

In Table 1 are listed the distribution coefficients of 30 metal ion species on DEAE-cellulose in the oxalate form as a function of oxalic acid concentration. The metals are arranged in the order of their distribution coefficients in 0.10*M* oxalic acid. A number of metal ions can be adsorbed on DEAE-cellulose sufficiently strongly to allow retention on a column from aqueous oxalic acid media, although only a very limited number of ions, such as Hg(II),[7] Au(III)[9] and

Table 1. Anion-exchange distribution coefficients of metals on DEAE (oxalate)-cellulose in oxalic acid media

Metal \ Oxalic acid, M	K_d 0.0010	0.010	0.030	0.10	0.30	0.50	Method**
Zr(IV)	$>3 \times 10^4$	$>3 \times 10^4$	$>3 \times 10^4$	$>3 \times 10^4$	9.3×10^3	2.7×10^3	a
Hf(IV)	3.1×10^3	5.5×10^3	1.3×10^4	1.4×10^4	7.3×10^3	2.3×10^3	a
Fe(III)	1.2×10^4	6.8×10^3	6.8×10^3	2.8×10^3	1.0×10^3	4.5×10^2	a
Ga(III)	3.1×10^3	3.1×10^3	3.1×10^3	2.1×10^3	6.9×10^2	3.2×10^2	a
Sn(IV)*	$>7 \times 10^3$	$>7 \times 10^3$	$>7 \times 10^3$	2.0×10^3	4.0×10^2	2.6×10^2	a
Ti(IV)	$>1 \times 10^4$†	8.2×10^3	4.0×10^3	1.8×10^3	5.6×10^2	3.3×10^2	a
U(VI)	1.7×10^4	1.0×10^4	4.8×10^3	1.3×10^3	3.5×10^2	1.4×10^2	a
Mo(VI)	4.1×10^3	2.8×10^3	2.3×10^3	9.4×10^2	3.2×10^2	1.8×10^2	a
Ge(IV)	$>3 \times 10^2$	$>3 \times 10^2$	$>3 \times 10^2$	$>3 \times 10^2$	2.9×10^2	1.5×10^2	b
Al(III)	1.8×10^3	2.0×10^3	7.6×10^2	6.9×10^2	1.8×10^2	1.0×10^2	a
In(III)	1.3×10^4	5.8×10^3	3.7×10^3	6.2×10^2	83	30	a
Bi(III)	ppte	ppte	ppte	4.2×10^2	74	33	a
V(IV)	5.3×10^3	3.1×10^3	1.3×10^3	3.2×10^2	67	40	a
W(VI)	4.7×10^3	1.7×10^3	8.1×10^2	2.3×10^2	1.0×10^2	73	a
Re(VII)	4.8×10^2	4.1×10^2	2.4×10^2	1.2×10^2	83	84	a
Sc(III)	1.1×10^3	7.6×10^2	4.3×10^2	1.1×10^2	19[b]	10[b]	a,b
Cu(II)	1.8×10^3	1.2×10^3	3.5×10^2	87	20	13	a
Se(VI)	$>3 \times 10^2$	$>3 \times 10^2$	$>3 \times 10^2$	52	15	10	b
Ni(II)	1.1×10^3§	3.5×10^2§	79§	14§	8	5	a
Hg(II)	90	54	13	9	6	6	b
Zn(II)	4.7×10^2	1.9×10^2	35	8.0[b]	3.1[b]	2.7[b]	a,b
As(V)	74	21	8.0	6.6	4.3	4.1	b
Se(IV)	70	12	8.6	5.1	4.5	3.2	a,b
As(III)	5.3	5.0	4.0	4.0	4.0	4.0	b
Co(II)	2.2×10^2	82	17	4	3	3	a
Te(IV)	5.8	3.1	2.5	2.5	2.1	2.1	b
Te(VI)	4.5	4.5	3.8	3.1	2.5	2.5	b
Cd(II)	18	5.5	2.0	2.0	1.5	1.5	b
Cr(III)	3.3	2.5	2.5	2.0	2.0	1.0	b
Mn(II)	9	2	<1	<1	<1	<1	a

* 0.001M H_2SO_4 present.
** a, batch method, b, column method.
† Measured in 0.0020M oxalic acid.
§ 2 μmole of Ni used.

some platinum group metals,[8] can be adsorbed on DEAE-cellulose from aqueous mineral acid or salt solutions. Pronounced adsorption from oxalic acid media is probably caused by the weak adsorption of oxalate and bioxalate anions on DEAE-cellulose, so that metal oxalato complexes do not compete strongly for exchanger sites.

Adsorption trends are such that the distribution coefficients decrease with increasing concentration of oxalic acid for the majority of metals listed in Table 1, while that of hafnium goes through a distinct maximum at 0.1M oxalic acid. As seen in Table 1, ter- and quadrivalent metals including Zr(IV), Hf(IV), Fe(III), Ga(III), Sn(IV), Ti(IV) and In(III) show significant adsorption over a wide range of oxalic acid concentration (<0.1M), thus allowing their separation from bivalent metals. Among the multivalent metals Al(III) and Sc(III) adsorb to a lesser extent, so that their adsorption sequences border those of Cu(II) (which shows the highest distribution coefficients among bivalent metal ions). Generally, the distribution coefficients of bivalent metal ions, including Cu(II), Ni(II), Zn(II), Co(II), Hg(II), Mn(II) and Cd(II), are one or two orders of magnitude lower than those of the ter- and quadrivalent metal ions, even though Cu(II) and Sc(III) behave similarly over the oxalic acid concentration range tested.

The adsorptions of U(VI), Mo(VI), V(IV) and W(VI) are also strong in accordance with the masking action of oxalate for these metal ions.[11] On the other hand, the adsorbabilities of the oxyanions of As(III), As(V), Se(IV), Te(IV) and Te(VI) are low, while that of selenate is high, as in formic acid media, where Se(VI) exhibits distribution coefficients high enough to allow the column separation of Se(VI) and Se(IV).[12]

De Corte *et al.*[3] have investigated the anion-exchange behaviour of 12 elements on Dowex 1 X-8 in oxalic acid solutions. With respect to 9 elements in common with the present study, *viz.* As(III), Mn(II), Co(II), Zn(II), Hg(II), Cu(II), In(III), Sc(III) and Mo(VI), the trend of their distribution coefficients was similar to that on DEAE-cellulose in oxalic acid media; the K_d values for the tervalent elements In(III) and Sc(III) are high relative to those for bivalent metals. As(III) and Mn(II) are weakly adsorbed and Mo(VI) exhibits a strong adsorption over the whole range of oxalic acid concentration studied. However,

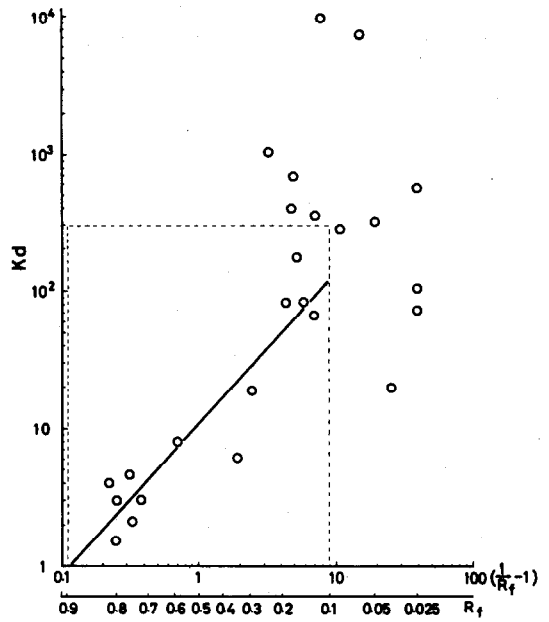

Fig. 1. Plot of log K_d against log $\{[(1)/R_f] - 1\}$. (The regression line of log K_d against log $\{[(1)]/R_f] - 1\}$ was based on the data present in the square defined by the x-axis and the dotted lines).

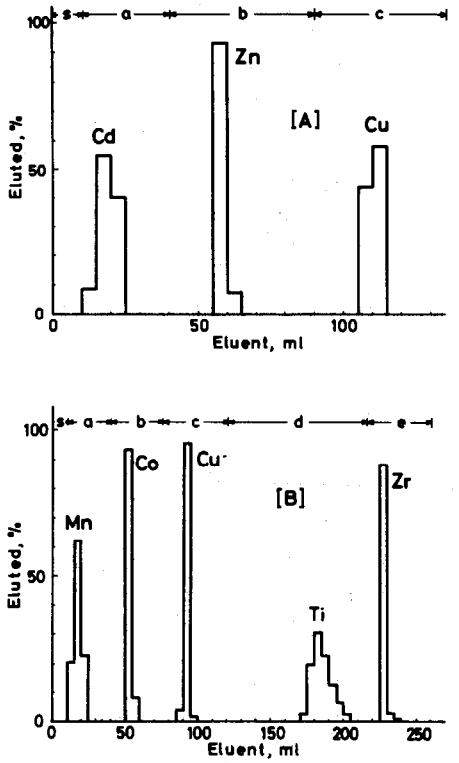

Fig. 2. Multicomponent separations. [A] s: sample, 0.01M oxalic acid solution. Eluents: a, 0.01M oxalic acid; b, 0.1M oxalic acid; c, 0.1M HCl. Cd(II) 507 μg, Zn(II) 198 μg and Cu(II) 252 μg added. [B] s: sample, 0.01M oxalic acid solution. Eluents: a, 0.01M oxalic acid; b, 0.1M oxalic acid; c, 0.5M oxalic acid; d, 0.03M oxalic acid, 0.1M HCl, 0.1% H_2O_2; e 3M HCl. Mn(II) 532 μg, Co(II) 228 μg, Cu(II) 202 μg, Ti(IV) 238 μg and Zr(IV) 488 μg added. Column: 13 mm bore × 8 cm; containing 1.0 g of DEAE-cellulose (oxalate). Flow-rate 1 ml/min.

the K_d values on Dowex are much higher and the selectivity sequences are not the same as for the DEAE-cellulose. In 0.03M oxalic acid the sequences are Mo(VI) ⩾ In(III) > Sc(III) ⩾ Cu(II) > Hg(II) > Zn(II) > Co(II) > Mn(II), As(III) on Dowex 1 and In(III) > Mo(VI) > Sc(III) > Cu(II) ⩾ Zn(II) > Hg(II) > Co(II) > Mn(II), As(III) on DEAE-cellulose.

The K_d ratios (Dowex/DEAE) are >43 for Mo(VI), 15 for In(III), 39 for Sc(III) and 35 for Zn(II). The adsorption of metals on DEAE-cellulose is moderate so the use of hydrochloric acid–oxalic acid media[1] significantly reduces the K_d values and column retention, except for a few metals such as zirconium and hafnium. This may be judged from the R_f trend on DEAE-cellulose in hydrochloric acid–oxalic acid media.[6]

In partition chromatography the relationship between the partition coefficient D and R_f can be given by the classical Martin and Synge equation:

$$D = \frac{A_m}{A_s}\left(\frac{1}{R_f} - 1\right) \quad (1)$$

where A_m and A_s are the cross-sectional areas of the mobile and stationary phases, respectively (assumed to be constant along the whole chromatogram[13]). The relationship has been extended to ion-exchange paper chromatography.[14,15] The logarithms of the distribution coefficients on DEAE-cellulose in 0.30M oxalic

Table 2. Separations

Element	Taken	Found	Eluent, *ml*	Sample volume, *ml*
Se(IV)	4.36 mg	4.38 mg	0.03M H_2Ox, 40	10
Se(VI)	4.67 mg	4.60 mg	1M HNO_3, 50	
As(III)	20.9 μg	21.1 μg	0.001M H_2Ox, 20	5
As(V)	38.5 μg	37.1 μg	1M HNO_3, 30	
Ti(IV)	714 μg	718 μg	H_2Ox mixture,† 105	10
Zr(IV)	2.13 mg	2.14 mg	3M HCl, 30	

Sample made up to simulate the first eluent composition.
† 0.03M in oxalic acid, 0.1M in HCl and 0.1% in H_2O_2.

acid are plotted in Fig. 1 against the logarithms of the function $\{[(1)/R_f] - 1\}$, R_f values being those previously reported for the same system.[6] As can be seen, points at higher adsorptions are scattered and no apparent correlation appears to exist between log K_d and log $\{[(1)/R_f] - 1\}$. This is because lower R_f values (less than 0.1) are difficult to determine accurately and correspond to a wide range of high distribution coefficients ($0.1 > R_f > 0$ may cover the coefficients from *ca.* 100 to infinity). Measurements of very high and very low distribution coefficients are also erratic. When the data are restricted to a region of moderate adsorption ($K_d < 300$ and $0.1 < R_f < 0.9$), the regression equation for log K_d against log $\{[(1)/R_f] - 1\}$ is

$$\log K_d = 1.10 \log\left(\frac{1}{R_f} - 1\right) + 1.03 \qquad (2)$$

with a correlation coefficient of 0.93. For similar plots in 0.01, 0.03 and 0.10*M* oxalic acid media, the slopes of the linear regression lines are 0.91, 0.72 and 1.01, respectively. The slopes are almost unity, so equation (1) holds for ion-exchange systems where moderate adsorption is taking place. The equation cannot be extended to obtain K_d values from extreme R_f values.

Inspection of the distribution coefficients given in Table 1 suggests that many separations of analytical interest can be achieved. In Table 2 are given the results for the separations of Se(IV)–Se(VI), As(III)–As(V) and Ti(IV)–Zr(IV) mixtures, which are usually difficult to achieve. Examples of multicomponent separations are shown in Fig. 2. Elution of each metal is sharply defined with no tailing.

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A NEW GRAPHIC METHOD FOR DIFFERENTIATING MONONUCLEAR AND POLYNUCLEAR COMPLEXES AND FOR DETERMINING THEIR STABILITY CONSTANTS

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Summary—A new graphical method is proposed for differentiating mononuclear and polynuclear complexes as well as for determining the stability constant of any complex A_mB_n. The method is based on the effect of dilution on the degree of dissociation of the complex. The resultant mathematical equation provides a simple graphical calculation which leads to the determination of the stability constant and also the molar absorptivity of the complex.

The method proposed in this paper provides for the differentiation of mononuclear and polynuclear complexes (e.g. AB and A_2B_2), as well as the determination of the stability constant for any complex of the form A_mB_n. The method is based on the effect of dilution on the degree of dissociation of the complex, a principle already used by several authors, notably Klausen[1] and Budĕšínský.[2-4] For a more thorough understanding, the reader should consult McBryde's excellent summary of spectrophotometric methods for determining equilibrium constants in solution.[5]

The calculation systems used by Klausen and Budĕšínský are similar, although somewhat awkward since they require curve-patterns that are valid only under fixed experimental conditions.

This difficulty is eliminated by the method proposed here. The basic advantage of this new method lies in the use of a mathematical equation which directly produces a simple graphic calculation of the stability constant and also of the molar absorptivity of the complex. Further, the equation gives a straight line, an ideal requirement for graphical methods.

We wish to emphasize that in this method mononuclear and polynuclear complexes are distinguished by a procedure as simple as that of differentiating between a straight line and a curve.

THEORY

Let us consider the complexation equilibrium

$$mA + nB \rightleftharpoons A_mB_n$$

where $(m,n \geqslant 1)$.

The stability constant is

$$K = \frac{[A_mB_n]}{[A]^m[B]^n} \quad (1)$$

Let a and b be the initial concentrations of A and B, respectively, and chosen so that $a/b = m/n$, and define the degree of complexation α_c, by the expression

$$\alpha_c = \frac{[A_mB_n]}{[A_mB_n]_{max}} = \frac{[A_mB_n]}{a/m} = \frac{[A_mB_n]}{b/n} = \frac{A}{A_{0(b)}} \quad (2)$$

where A is the absorbance difference between complex and reagent, and $A_{0(b)}$ the absorbance for complete complexation at reagent concentration b, *i.e.*, when $\alpha_c = 1$.

The complex and reagent concentrations in equilibrium will be:

$$[A_mB_n] = \frac{b}{n}\alpha_c$$

$$[A] = \frac{m}{n}b(1 - \alpha_c)$$

$$[B] = b(1 - \alpha_c)$$

Substituting these values into equation (1) and then simplifying gives

$$K = \frac{n^{(m-1)}\alpha_c}{m^m b^{(m+n-1)}(1 - \alpha_c)^{(m+n)}} \quad (3)$$

Replacing α_c by $A/A_{0(b)}$ and rearranging yields

$$\frac{A}{b^{(m+n-1)}} = \frac{Km^m A_{0(b)}}{n^{(m-1)}}\left(1 - \frac{A}{A_{0(b)}}\right)^{(m+n)} \quad (4)$$

Provided that the Lambert–Beer law is obeyed, when an initial concentration b_0 is diluted by a factor β, the corresponding value of $A_{0(b_0)}$ is decreased by the same factor:

$$b = b_0/\beta; \quad A_{0(b)} = A_{0(b_0)}/\beta$$

By substitution of b and $A_{0(b)}$ in equation (4) we can obtain:

$$\frac{\beta A}{(b_0/\beta)^{(m+n-1)}} = \frac{Km^m A_{0(b_0)}}{n^{m-1}}\left(1 - \frac{\beta A}{A_{0(b_0)}}\right)^{(m+n)}$$

Table 1.

Stoichiometry	Ordinate	Slope
1:1	$(\beta A)^{1/2}/(b_0/\beta)^{1/2}$	$(K/A_{0(b_0)})^{1/2}$
2:2	$(\beta A)^{1/4}/(b_0/\beta)^{3/4}$	$(2K/A^3_{0(b_0)})^{1/4}$
2:1	$(\beta A)^{1/3}/(b_0/\beta)^{2/3}$	$(4K/A^2_{0(b_0)})^{1/3}$
3:1	$(\beta A)^{1/4}/(b_0/\beta)^{3/4}$	$(27K/A^3_{0(b_0)})^{1/4}$

Finally, by extracting the $(m + n)$th root we obtain

$$\frac{(\beta A)^{1/(m+n)}}{(b_0/\beta)^{(m+n-1)/(m+n)}} = \left(\frac{Km^m A_{0(b_0)}}{n^{m-1}}\right)^{1/(m+n)}\left(1 - \frac{\beta A}{A_{0(b_0)}}\right) \quad (5)$$

A straight line is obtained by plotting the first term on the right of equation (5) against βA. When

$$\frac{b_0}{\beta} \to \infty, \quad \frac{(\beta A)^{1/(m+n)}}{(b_0/\beta)^{(m+n-1)/(m+n)}} \to 0$$

and

$$\beta A \to A_{0(b_0)}$$

That is, the intersection of this straight line with the abscissa provides the value of $A_{0(b_0)}$. The slope of the straight line,

$$\left(\frac{Km^m}{n^{m-1}A^{(m+n-1)}_{0(b_0)}}\right)^{1/(m+n)}$$

allows the calculation of the stability constant. The ordinates and slopes corresponding to different stoichiometries are given in Table 1.

The method proposed provides for the differentiation of mononuclear and polynuclear complexes and also the determination of the stability constants for these complexes. Suppose that the stoichiometry of a complex corresponds to a molar ratio equal to one. If a plot of $(\beta A)^{1/2}/(b_0/\beta)^{1/2}$ against βA does not give a straight line then $(\beta A)^{1/4}/(b_0/\beta)^{3/4}$ can be plotted and a straight line obtained in that case will confirm that the complex is 2:2. It can be proved that the ordinates for a 2:2 complex are the same as for a 3:1 complex but the slopes are different. Also, since work is always done at the stoichiometric ratio, secondary reactions which could occur when dealing with an excess of reagent or cation are avoided.

Though it is necessary to know the stoichiometry of the complex beforehand, in order to apply this method, the proposed procedure is useful for checking the stoichiometry obtained by any method. Nevertheless, this procedure is not valid if several complexes are formed at the same time. This is a disadvantage common to all spectrophotometric methods for determining constants.

Accuracy and precision of the method

The stability constant of a complex species can be obtained by means of equation (3). For a particular value of the concentration b, the expression $dK/Kd\alpha_c$ can give us the relative error of K with respect to the degree of complexation α_c. We can differentiate the expression from equation (3) to obtain

$$\frac{dK}{K\,d\alpha_c} = \frac{1 + (m + n - 1)\alpha_c}{(1 - \alpha_c)\alpha_c}$$

Let us consider a complex with 1:1 stoichiometry. By approximation to finite increments, the following expression is obtained:

$$\frac{\Delta K}{K} = \frac{1 + \alpha_c}{(1 - \alpha_c)\alpha_c} \cdot \Delta\alpha_c$$

The precision of the method then depends on the values α_c and $\Delta\alpha_c$, the latter being the precision of the measurement of α_c. Accepting a reasonable value of $\Delta\alpha_c$ as being ± 0.01 we can calculate the relative errors as a function of α_c. Data are presented in Table 2. As can be observed, the precision of $\log K$ is within ± 0.03 when the degree of complexation is 20–60%. The precision is further improved because $\log K$ is obtained from the average value of several spectrophotometric measurements.

On the other hand, as $dK/Kd\alpha_c \to \infty$ when $\alpha_c \to 1$, the method is not applicable to strong complexes.

Field of application

When the degree of complexation is about 85–90%, the precision in $\log K$ cannot be better than ± 0.1, so these α_c values must be considered the highest for which the method is applicable. From this consideration we can calculate, for different stoichiometries, the highest values of $\log K$ which can be determined by this method:

Stoichiometry	1:1	2:2	2:1	3:1
$\log (K/\epsilon^{m+n-1})$	3	7	4	6

where ϵ is the molar absorptivity of the complex. Values of ϵ of about 10^4 are usual for complexes with organic ligands, so values of $\log K$ up to 7, 19, 12 and 18, respectively, can be determined by the method.

EXPERIMENTAL

Procedure

Mixtures of A and B at stoichiometric ratios but different concentrations are prepared so that in each the ratio $a/b = m/n$. The absorbance of these mixtures is then

Table 2.

α_c	$dK/Kd\alpha_c$	$\Delta K/K$	$\Delta \log K$
0.0	∞	∞	∞
0.1	12.2	0.122	± 0.06
0.2	7.5	0.075	± 0.03
0.3	6.2	0.062	± 0.03
0.4	5.8	0.058	± 0.03
0.5	6.0	0.060	± 0.03
0.6	6.7	0.067	± 0.03
0.7	8.1	0.081	± 0.04
0.8	11.2	0.112	± 0.05
0.9	21.1	0.211	± 0.10
1.0	∞	∞	∞

Table 3. Fe(III)–Chrome Azurol S system at pH 3.40 ($b_0 = 2 \times 10^{-5} M$)

b_0/β [Fe(III)], M	βA	$\frac{(\beta A)^{1/2}}{(b_0/\beta)^{1/2}}$	$\frac{(\beta A)^{1/4}}{(b_0/\beta)^{3/4}}$	α_c, %
4×10^{-6}	0.196	221.3	7439	41.7
5×10^{-6}	0.229	214.0	6542	48.7
1×10^{-5}	0.313	176.9	4206	66.6
2×10^{-5}	0.378	137.5	2622	80.4
4×10^{-5}	0.411	101.3	1592	87.4
$[A_2B_2]_{max} = 10^{-5} M$	$A_{0(b_0)} = 0.470$	—	0.0	100.0

measured against reference solutions which contain identical concentrations of reagent, but no cation.

The method can also be carried out by preparing a mixture of A and B at the stoichiometric ratio but with a concentration having a suitable absorbance. This mixture, along with its respective reference solution, can then be diluted successively, for example until the volume is doubled. Each time it is diluted, it is necessary to add additional secondary reagents to keep the ionic strength constant: buffer solution, ethanol, *etc.* It is also important to assure that on dilution the equilibrium is reached quickly, as some complexes, one formed, slowly decompose. It is convenient to increase the cell path-length by a factor equal or proportional to the dilution factor. In this fashion, the value of βA is obtained directly.

Reagents

Orotic acid monopotassium salt solution. A $10^{-3} M$ solution was prepared by dissolving 0.1942 g of the Schuchardt product and diluting to 1 litre with demineralized water.

Anthrapurpurin solution (1,2,7-trihydroxyanthraquinone). A $10^{-3} M$ solution was prepared by dissolving 0.256 g of the Michrome product in the minimum of ammonia solution and diluting to 1 litre with demineralized water.

Cu(II) solution. Prepared by dissolving 24.954 g of Merck $CuSO_4.5H_2O$ in 1 litre of demineralized water and standardized iodometrically. A $10^{-3} M$ solution was prepared by dilution.

Ni(II) solution. Prepared from Merck $Ni(NO_3)_2.6H_2O$, and standardized with dimethylglyoxime. A $10^{-3} M$ solution was prepared by dilution.

Instruments

Beckman 25 spectrophotometer and Crison pH-meter 74.

Fe(III)–Chrome Azurol S system at pH 3.40.

Klausen and Langmyhr[6] determined the stoichiometry of this complex by the continuous variations method, finding maximal absorption at a molar ratio equal to one.

In Table 3 the experimental data used by Klausen[1] to show that a complex with 2:2 stoichiometry is formed are presented. In the same table the values of $(\beta A)^{1/2}/(b_0/\beta)^{1/2}$ and $(\beta A)^{1/4}/(b_0/\beta)^{3/4}$, corresponding to complexes with stoichiometries of 1:1 and 2:2 respectively, are also shown.

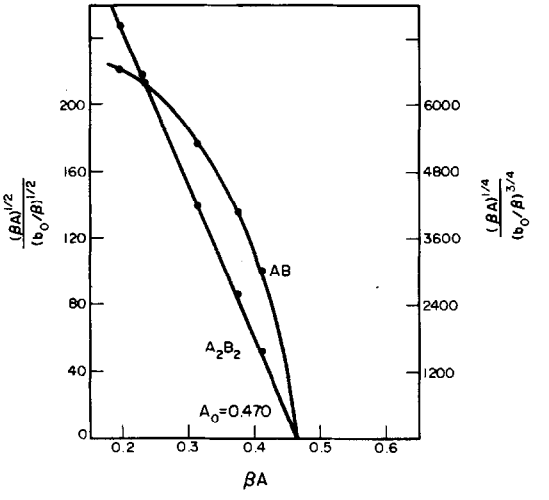

Fig. 1.

The values of $(\beta A)^{1/2}/(b_0/\beta)^{1/2}$ and $(\beta A)^{1/4}/(b_0/\beta)^{3/4}$ with respect to βA are presented graphically in Fig. 1, producing a curve and a straight line, respectively. This fact clearly indicates that the complex is 2:2 and not 1:1.

The intersection of the straight line with the abscissa gives a value of 0.470 for $A_{0(b_0)}$, which leads to a molar absorptivity of $0.470/10^{-5} = 4.70 \times 10^4$ l.mole^{-1}.cm^{-1} for the complex, and the α_c values which appear in Table 3.

By substitution of the values found for $A_{0(b_0)}$ and the slope of the straight line (2.73×10^4), in slope $= (2K/A^3_{0(b_0)})^{1/4}$ the stability constant of the complex can be calculated. In this manner, a value of 16.46 for $\log K$ is found, coinciding with that calculated by Klausen.

As can be observed, our method provides the same results as the Klausen method but in a very much easier way.

Table 4. Cu(II)–orotic acid system at pH 5.01 ($b_0 = 10^{-4} M$)

b_0/β [Cu(II)], M	A (310 nm)	βA	$\frac{(\beta A)^{1/2}}{(b_0/\beta)^{1/2}}$	$\frac{(\beta A)^{1/4}}{(b_0/\beta)^{3/4}}$	α_c, %
2×10^{-5}	0.064	0.320	126.5	2515	44.4
4×10^{-5}	0.162	0.405	100.6	1586	56.2
6×10^{-5}	0.265	0.442	85.8	1196	61.4
8×10^{-5}	0.385	0.480	77.4	984	66.7
1×10^{-4}	0.498	0.498	70.5	840	69.1
1.4×10^{-4}	0.735	0.525	61.2	661	72.9
2.0×10^{-4}	1.095	0.548	52.3	511	76.1
$[AB]_{max} = 10^{-4} M$	—	$A_{0(b_0)} = 0.720$	0.0	—	100.0

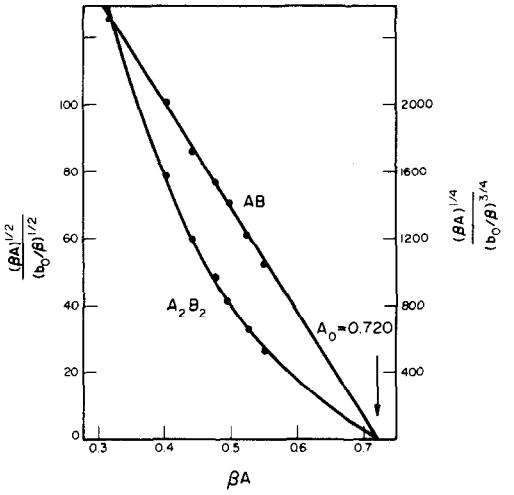

Fig. 2.

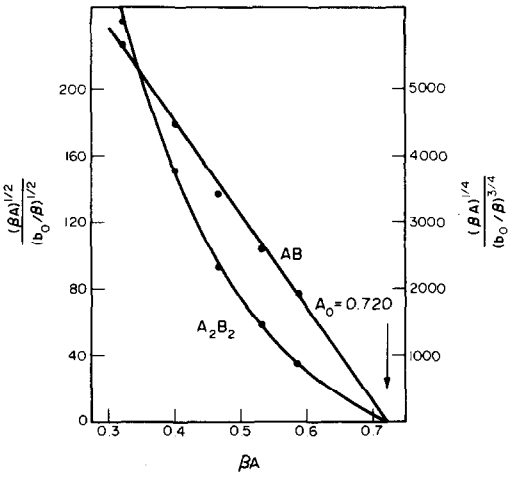

Fig. 3.

Cu(II)–orotic acid system

Capitán and Arrebola[7] determined the stoichiometry of this complex at pH 5.5 by various procedures, finding the existence of only one complex, of 1:1 stoichiometry.

The stability constant was determined at two pH values, 5.01 and 5.69, obtained with acetate buffers. The results obtained at pH 5.01 are presented in Table 4.

The values of $(\beta A)^{1/2}/(b_0/\beta)^{1/2}$ and $(\beta A)^{1/4}/(b_0/\beta)^{3/4}$ with respect to βA are presented graphically in Fig. 2, producing a straight line and a curve, respectively. This fact clearly indicates that the complex is 1:1 and not 2:2.

The value found for $A_{0(b_0)}$ gives a molar absorptivity of 7.2×10^3 l.mole^{-1}.cm^{-1} and the slope of the straight line (314) gives $\log K = 4.85$.

The corresponding results at pH 5.69 are presented in Table 5.

The corresponding graphical representation is shown in Fig. 3.

The slope of the straight line (562) gives $\log K = 5.35$; the molar absorptivity is the same as before.

Ni(II)–anthrapurpurin system at pH 9.73

The stoichiometry of this complex was determined by the continuous variations method; two complexes, with 1:1 and 1:2 stoichiometry [anthrapurpurin-Ni(II)], are formed successively.

The absorbances were measured 30 min after preparation of the solutions, in 1-cm cells. The results are shown in Table 6 for the complex of stoichiometry 1:2.

The value found for $A_{0(b_0)}$ gives a molar absorptivity of 5.50×10^3 l.mole^{-1}.cm^{-1} and the slope of the straight line (4055), gives $\log K = 9.86$.

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Table 5. Cu(II)–orotic acid system at pH 5.69 ($b_0 = 10^{-4}M$)

b_0/β [Cu(II)], M	A (310 nm)	βA	$\frac{(\beta A)^{1/2}}{(b_0/\beta)^{1/2}}$	$\frac{(\beta A)^{1/4}}{(b_0/\beta)^{3/4}}$	α_c, %
6.25×10^{-6}	0.020	0.320	226.2	6017	44.4
1.25×10^{-5}	0.050	0.400	178.9	3783	55.5
2.50×10^{-5}	0.116	0.464	136.2	2334	64.4
5.00×10^{-5}	0.265	0.530	102.9	1435	73.6
1.00×10^{-4}	0.585	0.585	76.5	874	81.2
$[AB]_{max} = 1.00 \times 10^{-4}M$	—	$A_{0(b_0)} = 0.720$	0.0	—	100.0

Table 6. Ni(II)–anthrapurpurin system at pH 9.73 ($b_0 = 1.2 \times 10^{-4}M$)

b_0/β [anthrapurpurin], M	A (590 nm)	βA	$\frac{(\beta A)^{1/3}}{(b_0/\beta)^{2/3}}$	α_c, %
7.5×10^{-6}	0.015	0.240	1622	36.4
1.5×10^{-5}	0.046	0.368	1178	55.7
3.0×10^{-5}	0.117	0.468	804	70.9
6.0×10^{-5}	0.265	0.530	528	80.3
1.2×10^{-4}	0.575	0.575	342	87.1
$[AB_2]_{max} = 1.2 \times 10^{-4}M$	—	$A_{0(b_0)} = 0.660$	0	100.0

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A SENSITIVE ATOMIC-ABSORPTION SPECTROMETRIC METHOD FOR THE DETERMINATION OF TIN WITH ATOMIZATION FROM IMPREGNATED GRAPHITE SURFACES

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Summary—The atomization of Sn from graphite surfaces is potentially hindered by reactions with the surface. The impregnation of graphite tubes with other carbide-forming elements (W, Zr, Ta, Mo) favourably alters the surface characteristics of the graphite furnace for the atomization of Sn. At the acid concentrations needed to prevent the hydrolysis of Sn, these surfaces are considerably more stable (even after more than 100 atomization cycles) than those of pyrolytic graphite. Two graphite furnaces of different design, the HGA 72 and the HGA 76, were tested. With impregnated graphite tubes the determination of Sn is possible in the HGA 72 with a detection limit of approximately 15 pg. In the HGA 76 the tin determination is vastly improved with respect to prolonged lifetime of the furnaces and stable signals over much longer periods of time. Detailed interference studies reveal that the use of the "gas stop" mode minimizes the influence of many ions that are frequently either introduced by the decomposition reagents or present in the sample itself. The practical potential of this method is demonstrated for the determination of Sn in a slag material and in copper- and aluminium-based alloys.

The determination of tin at trace levels is of great importance in organic as well as inorganic matter. Organo-tin compounds are frequently used as stabilizers for poly(vinyl chloride) resins used for packaging food items, but must be kept at a concentration of less than one part per million.[1] The tin content of inorganic matter affects, even at trace levels, the properties of alloys and thus it is desirable to monitor the concentration of tin at different stages of the production process. For tin, flame atomic-absorption spectrometry gives a reciprocal sensitivity of 0.15–3 ppm/1% absorption, depending on the resonance line and flame composition used.[2–4] Unfortunately, the 0.15 ppm/1% absorption value was measured at the 224.6 nm resonance line, a wavelength subject to interference. Early designs of the commercially available graphite atomizer could not be used for the determination of tin, presumably because of carbide formation.[5] As a result, Thomas and Thomerson[6] developed a method based on generation of stannane by borohydride; a similar method was later automated by Schmidt *et al.*[7] Although this method gave a reciprocal sensitivity of 0.44 ppm/1% absorption it is severely impaired by the instability of the evolved stannane.[8] As a result there is considerable interest in alternative methods, as is also indicated by the development of an indirect method based on the determination of Hg.[9] Recent versions of the graphite atomizer allowed the direct determination of tin in organic matter,[10,11] but in the only report of a tin determination in inorganic material[12] the results were inaccurate and sensitivities greatly reduced in decomposition solutions as compared to the sensitivity obtained in pure water. A recent study on determination of tin in steel[13] did not discuss possible interferences in a general sense and did not mention the effect of degradation of the graphite surfaces on the atomization signal, both of which were found to be very important by us as well as by Zatka.[14] As previously noted, alterations of the graphite furnace can lead to major changes in atomization characteristics, especially of refractory and carbide-forming metals.[15] The most widely advocated improvement concerns the use of pyrolytic graphite,[15–18] although impregnation procedures show distinct advantages as well.[14,19–21] In contrast to surfaces with pyrolytic graphite coatings, which have to be renewed frequently, the impregnated tubes show much better long-term stability with respect to sensitivity, without any significant degradation in precision.

This paper reports that the impregnation of graphite furnace surfaces leads to greatly improved sensitivity and/or less impairment from interferences, depending on the graphite atomizer design. The two atomizers studied were the HGA 72 and the HGA 76. A recently developed method for the simultaneous study of interferent effects[22] was utilized to ensure the significance of reported interferences. The effect

of impregnation is studied by scanning electron microscopy (SEM) and is discussed in terms of graphitization of the carbon induced by a carbide-forming metal, and the greater inertness of such a surface. The applicability of the method developed is shown by accurate analyses for tin in copper- and aluminium-based alloys and slag material.

EXPERIMENTAL

Impregnation studies

In preliminary experiments the effects of W, Ta, Mo, V, Zr, Ti and Si on the atomization of tin were studied. The graphite tubes were soaked overnight in the appropriate solutions, then dried at 120° for 2–4 hr.

Prior to the first determination, the impregnated tube was dried inside the graphite furnace for 1 min at 120°, for 30 sec at 400° and finally heated to 2200° within 90 sec by use of the programmable power supply, then kept at maximum temperature for 10 sec. This heating cycle was repeated twice.

The solutions used for impregnation are prepared as follows:

W-solution: 7.8 g of $Na_2WO_4 . 2H_2O$ dissolved in 100 ml of distilled water.

Ta-solution: 5 g of Ta powder dissolved in 25 ml of hydrofluoric acid (40% suprapur) by slow addition of 25 drops of nitric acid (65%) and made up to 100 ml with distilled water.

Mo-solution: 5 g of Mo dissolved in 200 ml of hydrochloric acid (30%) and 20 ml of nitric acid (65%), the solvent evaporated, the precipitated MoO_3 suspended in 50 ml of distilled water and dissolved by addition of solid sodium hydroxide. The solution is made up to 100 ml with distilled water.[23]

V-solution: 1 g of NH_4VO_3 dissolved in 84 ml of distilled water by slow addition of 16 ml of ammonia solution (25%).

Zr-solution: 5.8 g of $ZrOCl_2 . 8H_2O$ dissolved in 100 ml of distilled water.

Ti-solution: 1 g of Ti dissolved in 50 ml of hydrochloric acid (30%) by heating. After cooling, the solution is made up to 100 ml with hydrochloric acid (15%).

Si-solution: 4 g of sodium silicate (9-hydrate) dissolved in 95 ml of distilled water and 5 ml of hydrochloric acid (30%).

Tantalum hydroxide suspension:[24] 0.5 g of Ta powder dissolved in 2.5 ml of hydrofluoric acid (40% suprapur) by slow addition of 15 drops of nitric acid (65%), tantalum hydroxide precipitated by addition of solid sodium hydroxide and centrifuged. The precipitate is washed three times with distilled water and finally suspended in 3 ml of distilled water.

Instruments and apparatus

All impregnation studies were done with a Perkin–Elmer double-beam atomic-absorption spectrophotometer (model 403) in conjunction with the flameless atomization device HGA 72. The following were used as light-sources: an Intensitron hollow-cathode lamp and an electrodeless discharge lamp from Perkin–Elmer. The measurements were made at the 286.3 nm resonance line with a band-width of 0.7 nm. No corrections for broad-band absorption were made in the initial impregnation studies; in the interference experiments and in the subsequent analytical work a deuterium arc lamp was used for background correction. The signals were recorded on a Siemens Kompensograph III (250 μsec for 95% deflection) strip-chart recorder, for peak-height measurements. Argon was used as sheath gas. The interference studies and analyses were run on the Perkin–Elmer 403 and also on a Perkin–Elmer 420 in conjunction with the flameless atomizer HGA 76. The 403 instrument is equipped with a double-beam deuterium arc lamp background corrector. The sample delivery was handled by the Auto Sampling System AS1. A Perkin–Elmer 56 recorder (pen speed 500 μsec for 95% deflection) was used. Both peak heights and integrated absorbance values were recorded and evaluated. The argon purge-gas flow was set to 450 ml/min for the external gas stream, 145 ml/min for the internal purge gas stream and 25 ml/min for the "miniflow" option. The same light-sources, resonance line and band-width were used as for the Perkin–Elmer 403/HGA 72 system. All dilutions were made by using the Oxford microsampler system.

Interference studies

In an effort to simulate actual analytical situations, the interference experiments were carried out in a complex but rigorously controlled matrix. Multivariate statistical techniques were used to determine the effect of the single interfering species.[22]

Hydrochloric, nitric, sulphuric, phosphoric, perchloric and hydrofluoric acids were studied with respect to their influence on the signal for tin. These acids were chosen because their anions are frequently present in samples and the acids are also in use as decomposition reagents. It was decided to use a fractional design ($\frac{1}{2} \times 2^6$) to gain some insight into the presence and nature of interactions. Owing to the reduced experimentation compared to that for the full design (2^6), each main effect is confounded with a fifth-order interaction (*e.g.*, HCl and $HNO_3 \times H_2SO_4 \times H_3PO_4 \times HClO_4 \times HF$), each first-order interaction with a fourth-order interaction (*e.g.*, $HCl \times HNO_3$ and $H_2SO_4 \times H_3PO_4 \times HClO_4 \times HF$). The error was estimated from the confounded third-order interactions, the hypothesis being that these effects are negligible; this method gave 10 degrees of freedom for the error estimate, making the *F*-test fairly sensitive.

The matrix was, apart from the systematic variations in composition due to the experimental design, 5% v/v hydrochloric acid and 5% v/v nitric acid.

With the exception of nitric acid and hydrochloric acid all the lower concentration levels were chosen to be zero. The upper levels were 0.1 or 0.01*M* for the non-matrix acids, with the exception of phosphoric acid which was taken at 0.01 and 0.001*M* to avoid significant contamination and/or non-specific signals caused by that acid.

The reagents for the study of cationic interferences were made up according to the suggestions of the Perkin–Elmer handbook.[25] The elements studied included Al, Cu, Fe, Pb, Ni, Ca, Zn, Mg, Ba and Mn. The matrix was 5% v/v nitric acid; the relatively high concentration of this acid tended to obscure possible anionic effects of the counterions, but those will be discussed where appropriate. The concentrations of interferents were chosen in a 10–1000-fold weight ratio to tin. As the experimental effort for the study of all possible interactions was prohibitive, a minimal design confounding all the interactions was chosen.[26] This may have biased the estimation of some effects, but considering the general observation (from an earlier study) that interactions tend to exhibit much smaller effects than main factors,[27] this design should give a sufficient basis for further analytical work. The error estimate was derived from a replication, rather than from dummy variables.[22] This was deemed necessary since initial studies indicated the possibility of instrument drift. Within the blocks the experiments were run completely randomized. All calculations were done on the UNIVAC 494 computer of the Rechenzentrum Graz, using the program NYBMUL.[28]

Determination of tin in inorganic material

Metals and alloys were dissolved according to the methods given by Perkin–Elmer[25], with use of a previously

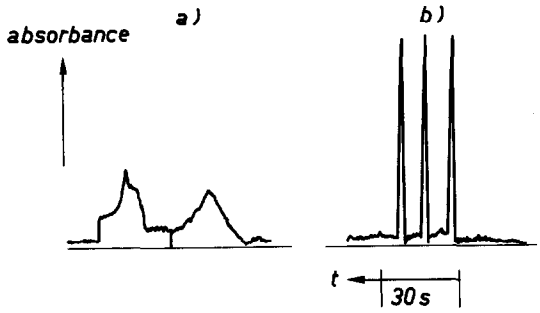

Fig. 1. Atomization of Sn from untreated and W-impregnated graphite furnaces (a) untreated, 125 ng of Sn; (*b*) W-impregnated, 10 ng of Sn. P.E. 403/HGA 72; hollow-cathode lamp; no gas-stop; 10% v/v HCl matrix; charring 1200°/30 sec; atomization at maximum temperature.

described mechanized system.[29] The amount used was adjusted to the expected concentration of tin and the solutions were diluted as necessary.

The slag material and the crude metal were decomposed under pressure in a closed PTFE vessel with 2 ml of nitric acid (65%) and 1 ml of hydrofluoric acid (40%) by heating at 180° for 75 min.[30] After cooling, the resulting solution was transferred to a saturated solution of boric acid (50 ml) at 80° and kept at that temperature for 30 min before dilution to volume.

Calibration was done with tin dissolved in 5% v/v hydrochloric acid or the decomposition solution. At lower concentrations of tin, the matrix of the calibration solution for copper-based alloys was matched to that of the sample solution by addition of appropriate amounts of copper.

Scanning electron microscopy (SEM) studies

The SEM studies were undertaken on a Jeol JSM 35 equipped with an energy-dispersive EDAX spectrometer (Si-crystal, 155 eV resolution, 400 channels). The acceleration voltage applied was 35 kV.

RESULTS AND DISCUSSION

Initial studies on the atomization behaviour of tin in the graphite furnace revealed very little sensitivity and poor precision.[5] This was attributed to the fact that tin forms a carbide stable enough to slow down considerably the mass transfer of the element to the gaseous phase, even at the highest operating temperature of the HGA 72 (2700°). Therefore, it was thought that a competitive reaction for the available free carbon sites on the surface of the furnace might improve the atomization. With W, V, Si, Mo, Zr, Ti and Ta as competitors in the formation of stable carbides, graphite furnaces were impregnated as described above. The concentrations of the impregnating solutions were optimized individually. Only for Ta was an alternative method of pretreatment considered: an aqueous tantalum hydroxide suspension (200 μl) was deposited through the sample introduction port and the furnace was conditioned by application of the heating cycle normally employed for the analysis.[24]

The solutions containing W, Mo, Zr and Ta gave positive results in these screening experiments, but V, Si or Ti solutions did not lead to a noticeable improvement. As an example, the effect of the sodium tungstate treatment is depicted in Fig. 1. Table 1 gives a summary of sensitivity and detection limit data in a 10% v/v hydrochloric acid matrix, as suggested by Perkin–Elmer.[25] The best precision was obtained with furnaces impregnated with sodium tungstate or zirconyl chloride; hence it was decided to study only these two reagents in more detail.

It was of particular interest to determine the long-term stability of the impregnated graphite furnaces. The sensitivity of several tungstate-treated furnaces was recorded over more than 150 atomization cycles and the first ten of these determinations were compared with the determinations after the first 100 cycles. Table 2 gives the results of such an experiment. Since the peak-height measurements are expected to be more sensitive than the integrated signals to

Table 1. Reciprocal sensitivity and detection limits for impregnated graphite furnaces

Impregnation	W	Ta	Mo	Zr	Ta hydroxide suspension
Reciprocal sensitivity *pg*/0.0044 *abs.u.*	25	33	45	90	40
Detection limit, HCL *pg* EDL	130	150	160	250	200
	13	16	18	30	20
R.S.D. at 1 ng Sn, %	4	12	7	2	18

P.E. 403/HGA 72; gas-stop mode; maximal atomization temperature; peak-height evaluation 10% v/v HCl matrix.

Table 2. Stability of tungstate-impregnated graphite furnaces

Number of detns.	Absorbance signals					Mean	Standard deviation	R.S.D., %
1–10	0.153	0.150	0.145	0.140	0.143			
	0.163	0.155	0.150	0.150	0.155	0.1504	0.0067	4.4
101–110	0.153	0.131	0.160	0.144	0.160			
	0.149	0.135	0.141	0.158	0.133	0.1464	0.0112	7.7

Sn 10 ng, hollow-cathode lamp, P.E. 403/HGA 72, no gas-stop, 10% v/v HCl matrix; temperature programme: 30 sec drying at 98°, 60 sec ashing at 500°, 10 sec atomization at maximal temperature.

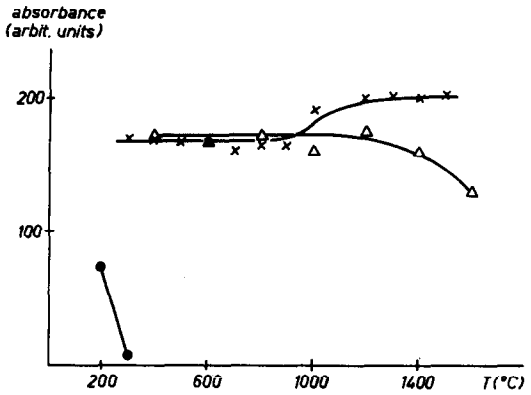

Fig. 2. Optimization of charring temperatures. ●——● 3% v/v H_2SO_4; ×——× 5% v/v HNO_3; △——△ 10% v/v HCl. P.E. 403/HGA 72; no gas-stop, 10 ng of Sn; charring time 30 sec, atomization at maximum temperature.

changes in the atomization behaviour, only these values are listed. Neither the *F*-test for the difference of variances, nor the *t*-test for the differences of mean values shows any significant change (95% confidence level) between newly impregnated and used impregnated furnaces. The reproducibility of the furnace impregnation process is within the experimental error of the determination itself.

Owing to the interactions of the tin and its counterion with the graphite, general data on thermal stability and volatility for different compounds are not easy to fit into consideration of the atomization. Therefore, an empirical approach was used for determining the maximal temperatures for the thermal pretreatment prior to atomization. Three acid matrices (nitric, hydrochloric and sulphuric) were chosen for this study all of them at a relatively high acid concentration (5%, 10% and 3% v/v respectively) to prevent the hydrolysis of tin. The determination of tin in sulphuric acid medium was impossible at all ashing temperatures (Fig. 2). The sensitivity was best for the nitric acid matrix if charring was done at temperatures above 1000°. This increase in sensitivity at higher charring temperatures is probably caused by the total volatilization of the remaining nitric acid which is found in graphite furnaces at temperatures as high as 1000–1100°.[15] Considerable decrease of the signal height is observed at 1200–1400°C for the hydrochloric acid matrix. The trend of these results is identical in the impregnated and non-impregnated HGA 76 furnaces, though the signal level was lower than with the impregnated HGA 72 furnace, because of the lower sensitivity.

Even though possible without impregnation, the determination of tin with the HGA 76 led to difficulties caused by the deterioration of signals after ~20 atomization cycles. A comparison of sensitivity data for the HGA 76 is given in Table 3. The increase in sensitivity due to impregnation is much less dramatic in this furnace, but it effectively prevents the attack of acids and leads to stable signals over more than 150 atomization cycles, as with the HGA 72 (Table 2).

SEM-studies were undertaken to explain the difference in atomization efficiency between the untreated HGA 72 and HGA 76 furnaces. As seen from Fig. 3, the structure of the graphite surfaces is quite different with respect to compactness. The HGA 72 furnace has a much rougher surface structure than the HGA 76 furnace, the latter being much better suited for the atomization of tin. This compact surface, however, is easily attacked by the relatively high acid concentrations and at high atomization temperatures, so that the SEM-picture of a used HGA 76 increasingly resembles that of the HGA 72 furnace as the number of atomization cycles increases. On a molecular basis it was suggested[31] that both the tin carbide formation and the subsequent "dissolution" of this compound in lower layers of the graphite during the ashing step are largely dependent on the carbon structure at the inner surface of the furnace. Apparently, the surface structure found for the HGA 76 furnace is at least initially less susceptible to these reactions with tin. For impregnated furnaces, these mechanisms occur largely for the elements used in the impregnation, as they serve as graphitization catalysts: the small graphite crystallites formed are non-reactive and slowly grow with continued heat treatment.[31] A change of the graphite surface could not be observed from the SEM-studies, although the porosity of the graphite seemed to increase considerably less for impregnated than for untreated furnaces with an increasing number of atomization cycles. As expected, the tantalum hydroxide treatment left a dense net of that reagent at the surface of the graphite, giving an entirely different topographic result from any of the impregnation procedures.

The influence of different anions was determined in the $\frac{1}{2} \times 2^6$ factorial experiment[13] is shown in Table 4. The most pronounced effect was caused by sulphuric acid and was attributed to the high volatility

Table 3. Reciprocal sensitivity for the determination of tin with the HGA 76

Gas-stop mode	Untreated	W-impregnation	Zr-impregnation
off	1300*	440	300
on	120*	70	80

* Rapid degradation of furnaces after ~20 determinations; all data in pg/0.0044 abs.u.

P.E. 420/HGA 76; maximal atomization temperature, peak-height evaluation; 10% v/v HCl matrix.

Fig. 3. SEM-pictures of untreated HGA-surfaces (400×) (*a*) HGA 72 (*b*) HGA 76

of tin sulphate. Independent of the matrix, phosphoric acid seems to lead to high tin signals if the gas-stop mode is not employed. In particular, the observation of an $H_2SO_4 \times H_3PO_4$ interaction makes the presentation of the data incomplete without a detailed examination of this second-order effect. Figure 4 shows a case where the $H_2SO_4 \times H_3PO_4$ interactions exceed the 95% confidence limit. Basically, it appears that the enhancement by phosphoric acid is observed only in the absence of sulphuric acid, but does not reverse the suppressive effect of sulphuric acid. The same is true for the interaction of perchloric acid and phosphoric acid. These interactions are an indication that the positive (H_3PO_4) and the negative (H_2SO_4 or $HClO_4$) influences are of a different nature. It appears that the enhancement is due to a more instantaneous volatilization whereas the low signals are most probably caused by pre-atomization losses.

A similar study for the HGA 76 showed interferences from sulphuric acid and phosphoric acid, and also from perchloric acid and hydrofluoric acid. As noted before, untreated graphite furnaces showed a strong degradation after a few atomization cycles. The $\frac{1}{2} \times 2^6$ experiment was therefore modified so that one degree of freedom was assigned to that degradation effect, leaving only 9 degrees of freedom for the estimation of the experimental error.[22] No degradation was found for W- and Zr-impregnated furnaces. The relative experimental errors for the results in Table 5 are 22, 18 and 11% for untreated, W- and Zr-impregnated furnaces, respectively. This is, of course, higher than expected for simple replications. It is also clear

Table 4. Interference of inorganic acids in the determination of tin with tungstate-impregnated graphite furnaces (HGA 72)

Matrix	HNO_3 5% v/v				HCl 5% v/v			
Amount of Sn, *ng*	1		10		1		10	
Concentration of acids, *M**	0.1	0.01	0.1	0.01	0.1	0.01	0.1	0.01
HCl	0	0	0	0	0	0	0	0
HNO_3	0	0	0	0	—	0	0	0
H_2SO_4	—†	—	—	—	—†	0	—†	0†
H_3PO_4 (0.01 and 0.001*M*)	0	0	+	+†	0†	0	+	+†
$HClO_4$	0	0	0	0	−†	0	0†	0
HF	0†	0	0	0†	0	0	0	0†
Gas-stop mode	on		off		on		off	

* The acid concentrations are given for non-matrix acids only; for HCl and HNO_3 this concentration has to be added to the concentration of the acid constituting the matrix.

† Interactions between acids significant.

Ar as sheath gas; 1200°/30 sec ashing, 10 sec atomization at max. temperature, peak-height measurements.

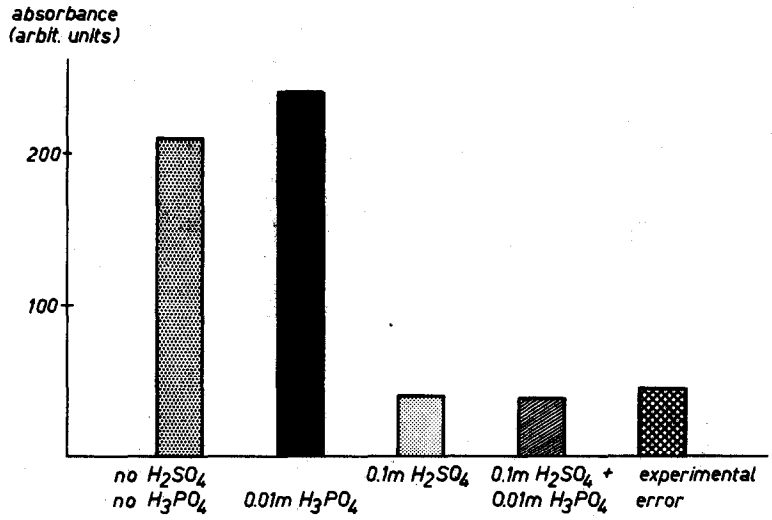

Fig. 4. Interaction of $H_2SO_4 \times H_3PO_4$ in the atomization of 10 ng of Sn. P.E. 403/HGA 72; W-impregnated graphite surface; no gas-stop; each bar represents the mean of 8 signals; the experimental error was estimated from 10 degrees of freedom; $\frac{1}{2} \times 2^6$ factorial design; charring 1200°/30 sec; atomization at maximum temperature.

from the data in Table 5 that integration of the signal does not eliminate these interferences; this was also noted by Sturgeon.[32]

Cationic interferences were studied for Ca, Zn, Mg, Ba, Cd, Mn, Al, Cu, Fe, Pb, Ni in 10–1000-fold ratio to tin, with tungstate-impregnated HGA 72 furnaces. These experiments were run for 10, 2 and 1 ng of tin without and with use of the gas-stop mode. For the concentrated (100 ppm) interference solutions in 1000-fold ratio to tin, the blanks were subtracted before the effects were calculated; this subtraction is the main reason for the increased experimental error. Since it was established earlier that no degradation of the furnace takes place over all 24 experiments, this experimental error could be calculated from paired observations (12 degrees of freedom). The effects are given in per cent of the signal obtained in the absence of the particular interfering species. The original study was done only with 10 ng and 1 ng of tin and gave many more interferences for 10 ng (without the gas-stop mode); this was somewhat surprising considering the fact that the weight ratio of interferents to tin was an order of magnitude smaller for the 10 ng of tin than for the 1 ng. For an intermediate amount of tin (2 ng), still in the linear range of the calibration curve for the gas-stop mode yet not too small to be measured without this mode, these interference studies were run again in presence of a 100-fold ratio of potential interferents to tin; again, the use of the gas-stop mode gave fewer interferences as well as a smaller relative standard deviation. According to L'vov and co-workers[33,34] the atomic population observed at the maximum of a peak is a function of the atomization time, τ_1, and the mean residence time of the atoms in the analysis volume, τ_2: for the commercial furnaces used the kinetic equations given[33,34] are only approximations.[32,35] For peak-height evaluations as used in Table 6 the constancy of the ratio τ_1/τ_2 is of instrumental importance for the signal observed. Changes

Table 5. Interference of inorganic acids in the determination of tin with impregnated and non-impregnated graphite furnaces (HGA 76)

Acids	Concentration, *M*	Impregnation of furnace: None peak	None integral	Tungstate peak	Tungstate integral	$ZrOCl_2$ peak	$ZrOCl_2$ integral
HCl	0.1	0	0*	0	0	0	0
H_2SO_4	0.1	–	–	–	–	–	–
H_3PO_4	0.01	+	+	–	0	–	0*
$HClO_4$	0.1	0	0	0	0	0	–
HF	0.1	0	0*	0	0	–	–
Degradation of furnace		strong		none		none	

* indicates significant interaction between different acids.
0 ... no influence at 95% confidence level.
– ... suppression.
+ ... enhancement.
Sn 1 ng in 5% v/v HNO_3; gas-stop mode on; ashing at 1200°/30 sec; 10 sec atomization at maximal temperature.

Table 6. Cationic interferences in the determination of Sn with the HGA 72

Amount of Sn, *ng*	10	1	2	2	10	1
Ratio (w/w) of interferent to Sn	100	1000	100	100	10	100
Ca	+12*	−13	−6	−5	—	—
Zn	−26	−31	−6	−5	—	−6
Mg	−12	—	—	—	—	—
Ba	+24	—	+10	—	—	—
Cd	−22	—	—	—	—	—
Mn	+21	−13	+10	—	—	—
Al	+71	+19	+19	+4	+17	—
Cu	—	—	—	—	—	—
Fe	−42	—	−20	−5	—	—
Pb	—	−13	−7	—	—	—
Ni	−45	—	−20	—	—	+9
Experimental error	12	12	7	3.5	10	7
Gas-stop mode	off	on	off	on	off	on
Blank subtracted	no	yes	no	no	no	no

* All data in %; Sn in 5% v/v HNO_3; Ar sheath gas; ashing 1200°/30 sec; EDL; maximal atomization temperature.

in τ_1 are most likely to be caused by the matrix, while τ_2 can be prolonged by working in the gas-stop mode. As long as $\tau_1/\tau_2 \ll 1$ little interference will be observed. Increasing the mean residence time makes the interference less severe; this is most likely what is observed in the experimental data of Table 6.

Subsequently, the investigations of cationic interferences in the HGA 76 were done only with use of the gas-stop mode. Here, the relative experimental error was determined by immediately replicated experiments. Again, the aging of the untreated furnace was quite apparent, as can be seen from Table 7. This aging not only decreases the sensitivity, as discussed in the description of anionic interferences, but makes the measurement much more susceptible to interferences; even though the concentrations of the interferents were an order of magnitude smaller, the interferences were more numerous and more pronounced. For the Zr-impregnation, no deterioration was found, as the interference tended to decrease with decreasing concentration of cationic species (Table 7).

To study the applicability of the method developed, several industrial samples were analysed with tungstate-impregnated furnaces in the HGA 72 (with which an analysis without impregnation had been totally impossible). The results (Table 8) agree well with the industrial analyses, showing the potential of the reported method.

All determinations were done in the gas-stop mode after appropriate dilution so that the linear portion of the calibration curve (up to 4 ng) could be used.

In summary, the impregnation of graphite furnaces with zirconium or tungstate improves the performance of the tin determination by electrothermal atomic-absorption spectroscopy, independent of the furnace design or graphite structure of the furnace. For porous graphite it enhances the sensitivity by 2–3 orders of magnitude; compact graphite surfaces are favourably altered, mainly with respect to their durability. Anionic and cationic interferences are less important when the preconditioning described is used. At the same time, the impregnation is easily carried

Table 7. Cationic interferences in the determination of Sn with the HGA 76

Ratio (w/w) interferent to Sn	Not pretreated				Zr-impregnated			
	1000		100		1000		100	
Measurement	peak	integral	peak	integral	peak	integral	peak	integral
Ca	—	—	−35	−57	—	—	—	—
Zn	—	—	−35	−58	—	—	—	—
Mg	—	—	−17	−51	—	—	—	−8
Ba	—	+23	—	+38	+17	+22	+10	+16
Cd	—	—	—	—	−23	−12	−13	−13
Mn	—	—	—	—	—	−12	—	—
Al	—	—	+52	+72	−16	—	−10	−13
Cu	−18	−16	+10	+29	−23	−19	—	—
Fe	−36	−22	−30	−71	−47	−36	−17	−13
Pb	—	—	−36	−58	−13	—	−6	—
Ni	−33	−26	−39	−69	−43	−36	−17	−23
Experimental error	23	18	11	22	9	12	6	9
Furnace age	new		used		new		used	
Blank subtracted	yes		no		yes		no	

All data in %; 1 ng of Sn in 5% v/v HNO_3; gas-stop mode; Ar sheath gas; ashing 1200°/30 sec; EDL.

Table 8. Results of tin determinations

Sample	Amount, *mg*	Calibrated against	Results ± standard deviation, *ppm**	Independent analysis, *ppm*†
Slag material	150	decomposition solution	1200 ± 50	1100
Crude Cu-metal	100	decomposition solution	1250 ± 70	1400
Cu-alloy	10	5% v/v HCl	980 ± 40	1000
Cu-alloy	200	5% v/v HCl & Cu	200 ± 15	210
Cu-metal	300	5% v/v HCl & Cu	10 ± 3	7
Al-metal	10	5% v/v HCl	4600 ± 300	5000
Al-metal	10	5% v/v HCl	10200 ± 400	9700

P.E. 403/HGA 72; W-impregnated furnace; gas-stop mode on; charring at 1200°/30 sec; peak-height measurements.

* Mean of 6.

† Data supplied by Dr. R. Pietsch and Dr. F. Frenzel.

out even under the conditions of routine analysis and should prove to be a simple and superior alternative to the hydride generation process or indirect determinations currently employed for the determination of tin in inorganic matter. The gas-stop mode should preferably be employed as it gives a higher sensitivity and less dependence on concomitant ions even at fairly high concentrations; a mechanism is proposed to explain this fact on the basis of L'vov's atomization equations. The agreement with independent determinations of tin in slag material, a mineral, and copper- and aluminium-based alloys shows that a direct determination is possible by matching the standard with the matrix element.

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KONZENTRIERUNG VON SPURENELEMENTEN DURCH EXTRAKTION MIT ALIPHATISCHEN MONOKARBONSÄUREN

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Zusammenfassung—Es wurden Faktoren untersucht, die die Abtrennung von Fe(III) durch Flüssig–Flüssig-Extraktion mit Caprylsäure beeinflussen. Die Extraktion von Fe(III) ist in Anwesenheit von Sulfat geringer als in Anwesenheit von Chlorid. Im Vergleich zu Natriumsalzen dominiert in Gegenwart von Aluminiumsalzen der Aussalzeffekt. Die thermodynamische Analyse der Verteilungsverhältnisse als Funktion verschiedener Konzentrationsparameter zeigt, daß Fe(III) als Dreikernkomplex extrahiert wird. Deshalb ist die Extrahierbarkeit bei großen Eisenmengen hoch, jedoch weniger befriedigend für Spurenmengen. Wenn Natriumcaprylat an Stelle der Säure verwendet wird, um Makromengen Eisen zu extrahieren, werden größere pH-Verschiebungen vermieden. Allerdings müssen substöchiometrische Mengen zugegeben werden, da sonst alle Metallionen nach einem einfachen Ionenaustauschmechanismus extrahiert werden. Die Bildung gemischter Komplexe von Eisen mit Kupfer und Nickel wurde nachgewiesen. Der Trennfaktor für diese Metallpaare ist deshalb unter bestimmten Bedingungen wesentlich geringer als durch das Verhalten der Einzelionen vorausgesagt wird. Cr(III) bildet ebenfalls gemischte Komplexe mit Fe(III), aber ihre Bildung ist kinetisch gehemmt. Aus diesem Grund sind Untersuchungen unter Gleichgewichtsbedingungen schwierig zu realisieren, aber bei kurzen Kontaktzeiten sind Trennungen möglich.

Das ständig wachsende Interesse an Reinststoffen stellt auch an die Analytik steigende Anforderungen. So liegen die heute geforderten Nachweisgrenzen für Spurenelemente in einer Matrix zwischen 10^{-5} und 10^{-10}%. Instrumentelle Direktverfahren sind in diesen Grenzbereichen sehr aufwendig und auf Grund des derzeitigen Kenntnisstandes in vielen Fällen auch stark fehlerbehaftet. Infolgedessen gewinnen kombinierte Bestimmungsverfahren, die chemische und physikalische Anreicherungstechniken einschließen, an Bedeutung.[1] Eine infolge ihrer schnellen und einfachen Handhabung sowie der zu erzielenden hohen Trenneffekte sehr verbreitete Methode zur Konzentrierung von Spurenelementen ist die Flüssig–Flüssig-Extraktion.[2] Dabei werden die verschiedensten Klassen von Extraktionsmitteln eingesetzt. Einerseits benutzt man selektive Extraktionsmittel zur quantitativen Abtrennung eines Elementes, und seine nachfolgende Bestimmung erfolgt individuell, oder man bedient sich solcher Extraktionsmittel, die eine Gruppenkonzentrierung zulassen. Man bestimmt dann die Verunreinigungen gemeinsam, z.B. durch Emissionssektralanalyse.

Aliphatische Monokarbonsäuren sind zur extraktiven Abtrennung sowohl des Matrixelementes als auch von Spurenelementen mit Erfolg anwendbar. Als kationenaustauschende Extraktionsmittel sind ihre Extraktionsgleichgewichte stark pH- abhängig. Das bedeutet, daß die Metallionen in Abhängigkeit von ihrer Basizität extrahiert werden und Trennungen sowie Konzentrierungen einzelner Elemente bzw. insbesondere von Elementgruppen durch die Wahl des pH-Wertes entsprechend der bekannten Reihe der abgestuften Extrahierbarkeit erfolgen können.[3] Auf Grund der Vielzahl von möglichen Einflußfaktoren und der daraus resultierenden Kompliziertheit derartiger Extraktionsgleichgewichte ist eine erfolgreiche Trennung und Konzentrierung nur möglich, wenn die Gesetzmäßigkeiten der Extraktionsreaktion genau bekannt sind.

Am Beispiel der Extraktion von Fe(III) mit n-Caprylsäure soll gezeigt werden, welchen Einfluß verschiedene Reaktionsparameter auf die Abtrennung des Eisens als Makro- bzw. Mikrokomponente haben.

EXPERIMENTELLES

Alle eingesetzten Verbindungen waren analysenrein. Durch Destillation wurden n-Caprylsäure und n-Dekan zusätzlich gereinigt. Lösungen von Natriumcaprylat in n-Caprylsäure wurden durch Eintragen von Na_2CO_3 in Caprylsäure erhalten.

Die Extraktionen wurden z.T. in 50-ml Schütteltrichtern durch mechanische Schüttlungen und z.T. in der Extraktionsapparatur AKUFVE 100 (MX Processer, Mölndal/Schweden) durchgeführt. Die Volumina in den

Schütteltrichtern betrugen jeweils für beide Phasen 10 ml, in der AKUFVE-Apparatur 450 ml. Die Temperatur betrug 25 ± 0,5°. Die pH-Werteinstellung erfolgte durch Zugabe von Natriumhydroxid bzw. entsprechender Mineralsäure. Die Metallkonzentrationen wurden in beiden Phasen radiometrisch durch Markierung mit ^{59}Fe, ^{64}Cu, ^{65}Ni und ^{51}Cr (Isocommerz GmbH, Berlin/DDR) bestimmt. Die Gleichgewichts-pH-Werte wurden mit einer Glaselektrode am pH-Meter MV 87 (VEB Präcitronic, Dresden/DDR) gemessen.

ERGEBNISSE UND DISKUSSION

Einfluß der Komplexbildung in der wäßrigen Phase auf die Extraktion

Einen entscheidenden Einfluß auf das Extraktionsgleichgewicht hat die Zusammensetzung der wäßrigen Lösung infolge von Komplexbildung und Hydrolyse der Metallionen. In Abb. 1 ist die Verteilung von Fe(III) in Abhängigkeit vom pH-Wert und vom Gehalt an Natriumsulfat dargestellt. Die Einführung von Sulfationen in das System führt auf Grund der Bildung von Sulfatokomplexen zur Verringerung der Konzentration an Fe^{3+}-Kationen und damit zur Erniedrigung der Fe(III)-Extraktion, so daß sich die Kurven im log *D*–pH-Diagramm mit steigendem Natriumsulfatgehalt nach rechts verschieben.

Abbildung 2 zeigt, daß bei der Extraktion von Fe(III) aus Aluminiumsulfat- bzw. Aluminiumchloridlösungen unterschiedlicher Konzentration unter ansonsten gleichen Bedingungen die Lage der Kurven zueinander im log *D*–pH-Diagramm im Vergleich zu den Experimenten mit Natriumsulfat verändert ist (auf Grund der geringeren Stabilität der Chlorokomplexe liegen die Kurven für chloridhaltige Lösungen im stärker sauren Bereich).

So nimmt bei niedrigen pH-Werten die Extrahierbarkeit des Eisens bei Zunahme der Aluminiumsulfatkonzentration zu. Dies ist die entgegengesetzte Erscheinung im Vergleich zu den Experimenten mit Natriumsulfat (vgl. Abb. 1), die entsprechenden Kurven im log *D*–pH-Diagramm verschieben sich nach links. Offensichtlich führt die stark aussalzende Wirkung der Aluminiumsalze bei niedrigen pH-Werten [für $AlCl_3$ pH < 1, für $Al_2(SO_4)_3$ pH < 2,1] zu dieser Verschiebung. Im weiteren Kurvenverlauf wirkt sich die gleichzeitige Extraktion von Aluminium und die damit verbundene Abnahme der Extraktionsmittelkonzentration sowie die Hydrolyse des Eisens[4] erniedrigend auf die Fe(III)-Extraktion aus. Bei Erhöhung des pH-Wertes streben die Verteilungsverhältnisse D_{Fe} einem Maximum zu, das mit steigender Aluminiumkonzentration sinkt.

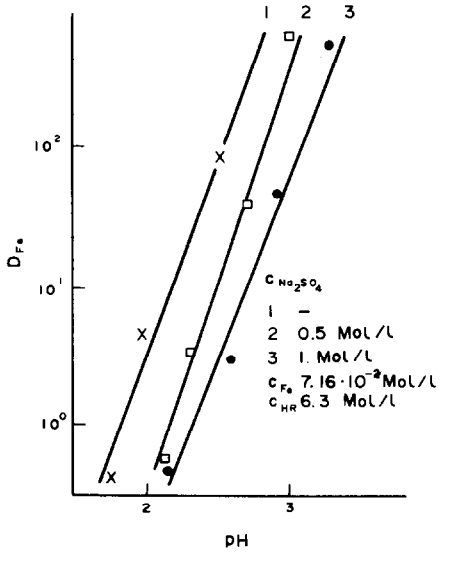

Abb. 1. Extraktion von Fe(III) mit n-Caprylsäure bei unterschiedlichen Gehalten an Na_2SO_4.

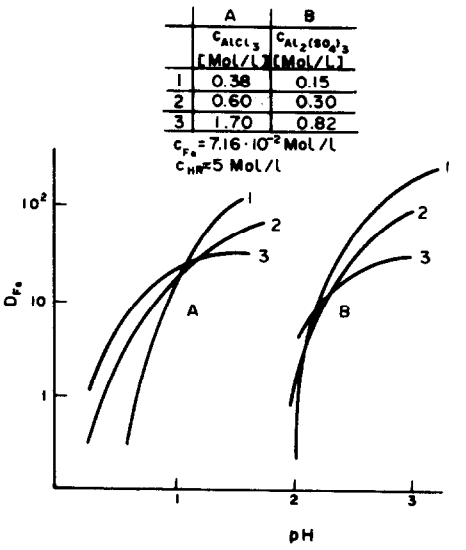

Abb. 2. Extraktion von Fe(III) mit n-Caprylsäure bei unterschiedlichen Gehalten an $AlCl_3$ bzw. $Al_2(SO_4)_3$.

Einfluß der Wechselwirkung in der organischen Phase auf die Extraktion

Bei der Abtrennung von Eisenspuren aus Alkali-, Erdalkali- oder Aluminium-salzlösungen ist zu berücksichtigen, daß sich in weiten Konzentrationsbereichen 3-Kern-Komplexe bilden.[5] Das Extraktionsgleichgewicht wird dabei durch Gleichung (1) beschrieben:

$$3Fe^{3+}_{(w)} + 3H_2O + \tfrac{9}{2}(HR)_{2(o)} \rightleftharpoons (FeR_3 \cdot H_2O)_{3(o)} + 9H^+_{(w)} \quad (1)$$

Im Unterschied zu idealen Systemen führt die Polymerisation der extrahierten Verbindung zu einer direkten Abhängigkeit des Verteilungsverhältnisses *D* von der Metallkonzentration $c_{Fe(w)}$.

Gleichung (2) zeigt die entsprechende quantitative Beziehung im vorliegenden Fall:

$$\log D_{Fe} = \log K_{Ex} + 9\,pH + 2\log c_{Fe(w)} - 3\log \Phi + \tfrac{9}{2}\log c_{HR_{(o)}} \quad (2)$$

Die Komplexierungsfunktion Φ gestattet bei der quantitativen Auswertung der Gleichung (2) die

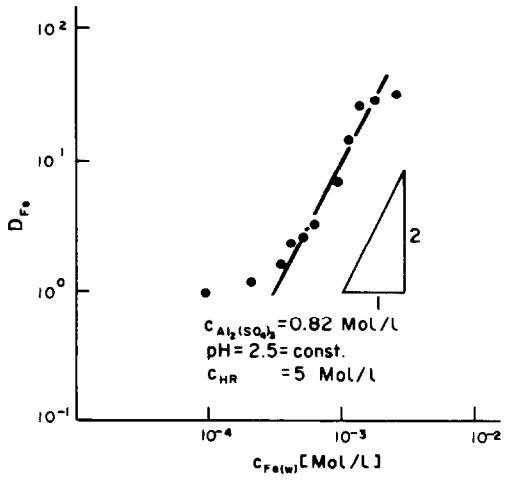

Abb. 3. Abhängigkeit der Fe(III)-Extraktion mit n-Caprylsäure von der Konzentration an Fe(III) in der wäßrigen Phase.

Berücksichtigung der Komplexbildung und Hydrolyse in der wäßrigen Phase.[5]

Die bestehende Proportionalität zwischen dem Verteilungsverhältnis D_{Fe} und der Eisenkonzentration $c_{Fe(w)}$ führt bei Verringerung der Fe-Konzentration zu kleineren D_{Fe}-Werten und damit zu einem Mehraufwand im Falle einer vollständigen Abtrennung. Abbildung 3 veranschaulicht diese Tatsache am Beispiel der Entfernung von Fe(III) aus konzentrierter Aluminiumsulfatlösung.

Abtrennung von Verunreinigungen vom Hauptbestandteil Eisen, ihre Konzentrierung und Bestimmung. Neben der Abtrennung von kleinen Eisenmengen ist es auch möglich, zur Bestimmung der Bestandteile in Stählen, von Verunreinigungen in reinem Eisen oder Eisenverbindungen das Matrixelement Eisen durch Extraktion mit Monokarbonsäuren soweit zu entfernen, daß die Begleitelemente in der verbleibenden wäßrigen Lösung bestimmt werden können. Wenn man jedoch Makromengen Eisen(III) extrahieren will, so werden bei der Extraktion mit Karbonsäure gemäß Gleichung (1) Wasserstoffionen frei, und der Übergang von Eisen wird vermindert. Die Verwendung von Natriumcaprylat als Extraktionsmittel und die Durchführung einer Austauschextraktion zwischen Na^+ und Fe^{3+} ermöglicht die Einstellung des gewünschten pH-Wertes für eine optimale Eisenextraktion. Zweckmäßigerweise verfährt man so, daß man das Natriumcaprylat in geringem stöchiometrischen Unterschuß wählt, da, wie in Abb. 4 zu sehen ist, im Bereich stöchiometrischer Verhältnisse ein starker Einfluß der Konzentration der Makrokomponente zu beobachten ist.[6]

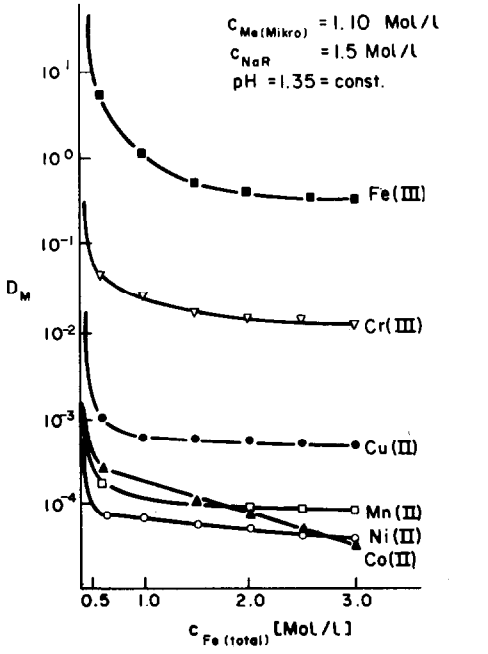

Abb. 4. Abhängigkeit der Verteilung von Fe(III) und verschiedenen Verunreinigungselementen von der Gesamtkonzentration an Fe(III) bei der Extraktion mit Natriumcaprylat.

Ein Überschuß des Extraktionsmittels führt dazu, daß alle metallischen Verunreinigungen gegen das Na^+ der Na-Seife ausgetauscht werden und damit eine Abtrennung nicht möglich ist. Im Bereich leichter Unterstöchiometrie an Extraktionsmittel, also bei Fe(III)-Überschuß, gibt es einen sehr starken Abfall der Verteilungsverhältnisse der Verunreinigungselemente, und zwar entsprechen diese in ihrer Abstufung der Reihe der Extrahierbarkeiten.

Abbildung 4 zeigt, daß sehr hohe Abreicherungsfaktoren z.B. für Nickel, Kobalt bzw. Kupfer erhalten werden. Größere Überschüsse an Eisen gegenüber der stöchiometrischen Extraktionsmittelkonzentration führen zu höheren Eisenmengen in der wäßrigen Phase und damit zu einer Verringerung der Konzentrierung, ohne daß die Trenneffekte wesentlich erhöht werden.

Die in der wäßrigen Phase verbliebenen Verunreinigungen können auf verschiedene Weise analysiert werden. Die optische Emissionsspektralanalyse bietet als typisches Übersichtsverfahren die Möglichkeit, das Verunreinigungskonzentrat ohne weitere Trennung zu untersuchen.[7] Hierbei werden definierte Mengen einer Indiumlösung als "innerer Standard" und Natriumchlorid zur Bogenstabilisierung auf die Trägerelektrode gebracht. Die Zugabe von Natriumchloridlösung zur Bogenstabilisierung kann entfallen, wenn die Extraktionsbedingungen so gewählt werden, daß die in 10 μl Analysenlösung enthaltene Natriummenge zwischen 30 μg und 100 μg liegt. In der Regel liegen die Natriumgehalte dann allerdings höher, so daß durch eine nachgeschaltete Trennoperation der Natriumgehalt verringert werden muß, wobei, wenn es sich beispielsweise um ein Ionenaustauschverfahren handelt, eine weitere Konzentrierung der Spurenelemente erreicht werden kann.

Das Endbestimmungsverfahren zur Untersuchung solcher Spurenkonzentrate[8] liefert die in Tabelle 1

Tabelle 1. Erfassungsgrenzen c_E in salzsaurer Lösung

Element	c_E, *ng*	Element	c_E, *ng*
Mg	3*	Mo	0,54
Al	1*	Ag	0,013
Si	10*	Cd	5,3
Ca	3*	Sn	3,0
Ti	0,25	Sb	40
V	0,24	La	10†
Cr	0,56	Ce	30†
Mn	0,4	Nd	10†
Co	0.9	Ta	10,0
Ni	1,1	Hf	4,0
Cu	0,1*	W	6,8
Zn	4,8	Re	6,4
Zr	0,74	Pb	3,0
Nb	1,5	Bi	1,0

* Erfassungsgrenze durch Blindwert bedingt.
† Erfassungsgrenze durch Bande bedingt.

angeführten Erfassungsgrenzen. Bei einigen Elementen werden diese Grenzen durch die Chemikalienblindwerte gegeben, obwohl destillativ gereinigte Chemikalien eingesetzt und stets in einer Reinluftbox gearbeitet wurde.

Bildung von heterogenen Mehrkernkomplexen. Schwierigkeiten bei der Trennung von Metallionen können auftreten, wenn es zu Wechselwirkungen zwischen den Metallen in der organischen Phase kommt.

In Abb. 5 sind experimentelle Ergebnisse zur Extraktion von Fe(III) und Cu(II) mit n-Caprylsäure aus sulfathaltigen Lösungen zusammengestellt. Die Kurven 1 und 2 wurden für Kupfer und Eisen allein erhalten. Bei gleichzeitiger Anwesenheit beider Metalle ergeben sich die Kurven 3 und 4. Es kommt bei gemeinsamer Anwesenheit zu einer deutlichen Erhöhung der Kupferverteilung und damit zur Erniedrigung der Trennfaktoren durch Bildung gemischter Cu–Fe-Komplexe in der organischen Phase. Beispielsweise erhöht sich die Cu-Extraktion bei einem pH-Wert von 2,75 von $1 \cdot 10^{-3}$ auf $1 \cdot 10^{-1}$%, also um den Faktor 100.

Durch thermodynamische Analyse entsprechender Verteilungsuntersuchungen erhält man, ausgehend von der Reaktionsgleichung (3):

$$x\mathrm{Cu}^{2+}_{(w)} + x(\mathrm{HR})_{2(O)} + (\mathrm{Fe_3R_9})_{(O)} \rightleftharpoons (\mathrm{Cu_xFe_3R_{9+2x}})_{(O)} + 2x\mathrm{H}^{+}_{(w)} \quad (3)$$

über die Beziehung (4):

$$\log c_{\mathrm{Cu(Fe)}} - \log c_{\mathrm{Fe(O)}} = \log \bar{K}_{\mathrm{Cu(Fe)}} + x\{2\,\mathrm{pH} + \log c_{\mathrm{Cu(w)}} + \log c_{\mathrm{HR(O)}}\} \quad (4)$$

die Zusammensetzung des Komplexes.

In diesem Falle konnte durch graphische slope-Bestimmung für den gemischten Komplex die Formel $\mathrm{CuFe_3R_{11}}$ ermittelt werden.

Zur Bildung derartiger gemischter Metallkomplexe in der organischen Phase kommt es auch bei der Extraktion von Fe(III) und Ni(II) mit n-Caprylsäure.[9] Die entsprechenden Extraktionskurven sind in Abb. 6 dargestellt.

Wechselwirkungen in der organischen Phase beo-

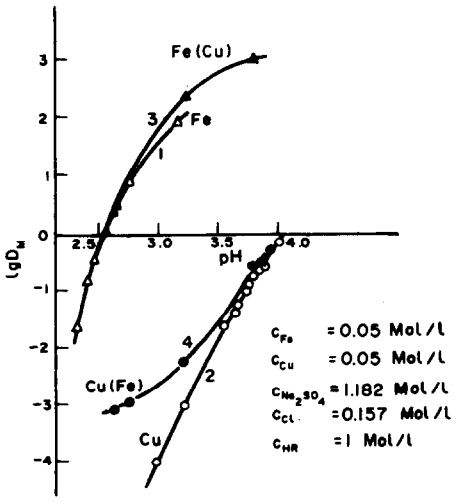

Abb. 5. Extraktion von Fe(III) und Cu(II) allein (Kurven 1 und 2) bzw. bei gemeinsamer Anwesenheit (Kurven 3 und 4) mit n-Caprylsäure.

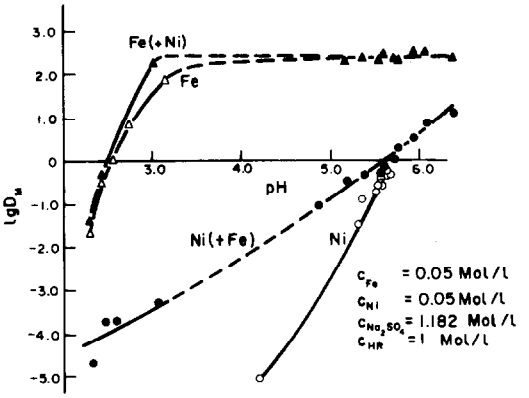

Abb. 6. Extraktion von Fe(III) und Ni(II) allein bzw. bei gemeinsamer Anwesenheit mit n-Caprylsäure.

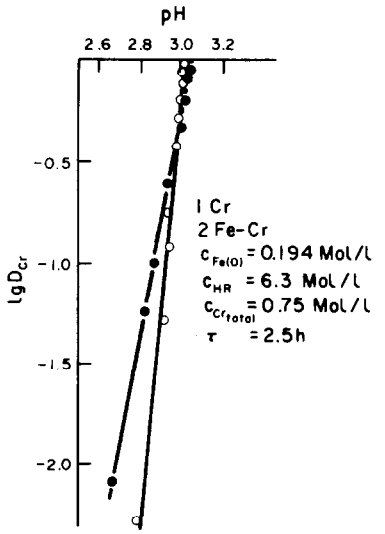

Abb. 7. Extraktion von Cr(III) allein (Kurve 1) bzw. bei Anwesenheit von Fe(III) (Kurve 2) mit n-Caprylsäure.

bachtet man auch bei der geichzeitigen Anwesenheit von Chrom und Eisen. Wie Abb. 7 zeigt ergeben sich Erhöhungen der Verteilungsverhältnisse für Cr(III) durch Extraktion eines gemischten Komplexes. Im vorliegenden Fall werden bei pH 2,7 aus einer 0,75 *M* Cr(III)-Lösung bei einstufiger Extraktion etwa 1%, also 7 mMole des Cr(III) in die organische Phase extrahiert. Bei Anwesenheit von 0,194 Mole Fe(III) werden 10% des Cr(III) extrahiert, wodurch in der organischen Phase ein Fe–Cr-Verhältnis von 2,5:1 entsteht. Die Chromextraktion ist allerdings kinetisch gehemmt, so daß dieser Effekt teilweise wieder aufgehoben wird, wenn man mit kurzen Kontaktzeiten ($\leq$ 15 min) arbeitet.

Schlußbemerkungen

In der vorliegenden Arbeit wurde versucht, durch Untersuchung einer relativ komplizierten Extraktionsreaktion einige Effekte anzugeben, die Konzentrierungsreaktionen beeinflussen und ihren Erfolg vermindern oder gar verhindern können. Die Bildung homogener Mehrkernkomplexe führt grundsätzlich zur Erhöhung des Aufwandes, wenn Spurenkozentrationen abgetrennt werden müssen. Die Bildung heterogener Mehrkernkomplexe kann Spurenabtrennungen ganz verhindern. Bei Kenntnis des Gesamtsystems lassen sich jedoch meist Gebiete finden, wo die Bildung solcher gemischter Komplexe nicht stattfindet oder keinen Einfluß auf die Trennung hat. Dies ist besonders dann der Fall, wenn sich der basische Charakter der zu trennenden Elemente sehr unterscheidet. Kinetische Hemmungen führen zu Schwierigkeiten bei quantitativen Auswertungen, lassen jedoch mitunter Trennungen für Metallpaare zu, die im Gleichgewicht nicht voneinander zu trennen sind.

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Summary—Factors affecting the separation of iron(III) by solvent-extraction with n-caprylic acid have been investigated. The extraction of iron(III) is diminished more in the presence of sulphate than of chloride, owing to the formation of complexes, while with aluminium salts, when compared with sodium salts, a salting-out effect predominates. Thermodynamic analysis of the change in distribution coefficient as a function of various concentration parameters has shown that the iron(III) is extracted as a trinuclear complex: the extractability is therefore better for larger amounts of iron, and less satisfactory for trace amounts. When sodium caprylate is used instead of the acid to avoid large pH changes when macro-amounts of iron are to be extracted, a substoichiometric amount must be added, otherwise all the metal ions will be extracted by a simple ion-exchange mechanism. Evidence is also presented for the formation of mixed complexes of iron with copper and with nickel: the degree of separation for these pairs of metals is therefore much less than would be predicted from the behaviour of the individual ions. Chromium(III) also forms a mixed complex with iron, but as its formation is kinetically inhibited, investigations under equilibrium conditions are difficult to realize. However, if the extractions are carried out quickly, with only short contact times, the separation of iron from chromium is hardly affected.

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N-SUBSTITUTED PHENOTHIAZINES AS REDOX INDICATORS IN BROMATOMETRY

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Summary—Diethazine hydrochloride, butaperazine dimaleate, trifluoperazine hydrochloride, promethazine hydrochloride, prochlorperazine maleate and chlorpromazine hydrochloride have been studied as indicators in bromate titration of quinol, metol and ascorbic acid. They give a very sharp reversible colour change at the equivalence point. Their formal potentials have been determined. A simple but accurate method for the estimation of quinol and metol is reported.

About ten reversible organic redox indicators have been proposed for bromate titrations, although numerous organic dyestuffs have been used as irreversible bromometric indicators. Most of the proposed reversible indicators are unsatisfactory for one reason or another. α-Naphthoflavone[1] forms a brownish precipitate with free bromine liberated at the end-point. *p*-Ethoxychrysoidine[2] gives a variable blank and its reversal cannot be repeated more than twice. Quinoline Yellow[3] gives a very faint colour change and the blank is rather high. Ferroin,[4] which requires high temperature (40–50°) and catalysts (osmic acid or sodium vanadate), gives sluggish end-points. Fuchsine[5] acts reversibly only at boiling temperature. The colour of 2,6-dichlorophenolindophenol[6] at the end-point is immediately destroyed by the addition of a drop of bromate. We have now found the optimum conditions for the direct titration of quinol, metol and ascorbic acid with potassium bromate, using diethazine hydrochloride (DH), butaperazine dimaleate (BPDM), trifluoperazine hydrochloride (TFP), promethazine hydrochloride (PH), prochlorperazine maleate (PCPM) and chlorpromazine hydrochloride (CPH) as reversible redox indicators.

EXPERIMENTAL

Reagents

Indicator solutions. All reagents were analytical-grade chemicals. Aqueous solutions (0.2% w/v) of DH, BPDM, TFP, PH, PCPM and CPH were prepared and stored in amber bottles. BPDM and PCPM were dissolved in hot water (60°).

Potentiopoised solutions. Equimolar vanadate–vanadyl potentiopoised solutions in 0.00625–6.0 *M* sulphuric acid were prepared.[7,8]

Reductants. Approximately 0.05 *M* solutions of quinol, metol and ascorbic acid were prepared by dissolving the requisite quantity of material in 0.04 *M* and 1 *M* sulphuric acid and 0.01% EDTA solution respectively. The quinol and metol solutions were standardized with ceric sulphate[9] and the ascorbic acid with potassium iodate.[10] The solutions were stored in amber bottles and diluted as required.

Determination of formal potentials

Ten-ml portions of the potentiopoised vanadate-vanadyl solutions were mixed with 0.5 ml of indicator solution, and the average of the potentials of the two solutions bracketing the colour change was taken as the formal redox potential. Schilt's method[11] was also used. The results are presented in Table 1.

Titration procedures

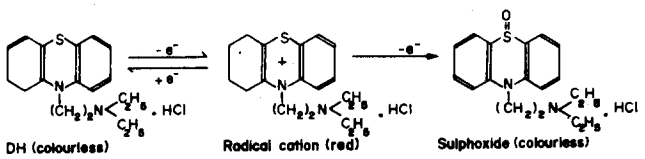
Quinol and metol. Take 20 ml of 0.05–0.01 *M* quinol, 10 ml of 10% potassium bromide solution and enough hydrochloric or sulphuric acid to give a concentration of 0.6 *M* (0.3 *M* sulphuric acid for CPH) at the end-point, and dilute to 40 ml. Titrate with 0.025–0.005 *M* potassium bromate to an orange-red, using 1 ml of 0.2% DH, BPDM, TFP, PH, PCPM or CPH added near the end-point (after 95% titration). For titration of 0.005–0.0025 *M* quinol, dilute 10 ml of sample, the acid and 3 ml of 10% potassium bromide solution to 25 ml and titrate with 0.0025–0.00125*M* potassium bromate, adding 0.5 ml of the indicator towards the end-point. In the titration of metol, use 1*M* sulphuric or 0.5*M* hydrochloric acid medium and 1 ml of 0.2% DH, BPDM, TFP or PH near the end-point.

Ascorbic acid. Take 20 ml of 0.05–0.025 *M* ascorbic acid, 10 ml of 10% potassium bromide solution and enough acid to give a concentration of 1.5 *M* hydrochloric acid (0.8 *M* for PCPM and CPH) or 1 *M* sulphuric acid at the end-point, and titrate as the mixture for quinol.

RESULTS AND DISCUSSION

DH, TFP, PH, PCPM and CPH are highly soluble in water, giving colourless solutions. BPDM gives a light yellow solution in water. The aqueous solutions are stable for about 3 days at room temperature (27°) and for about 2 months in an amber bottle at low temperature (8°); they slowly undergo photochemical oxidation to give a pale pink colour, but this does not interfere in their indicator action. They undergo one-electron reversible oxidation to a red intermediate which is believed to be a radical cation.[12] The radical cation is further oxidized irreversibly by excess of oxidant to a colourless sulphoxide, with the loss of one electron.[13,14] The mechanism of oxidation

of DH can be represented as follows:



The mechanism of oxidation of BPDM, TFP, PH, PCPM and CPH is similar. The formal potential of PCPM has already been reported to be 0.795 V,[15] that of CPH 0.799 V,[16] of PH 0.883 V,[17] and of DH 0.856 V.[8]

Titrations

Quinol. Kolthoff[18] reported that the end-point of the potentiometric titration of quinol with potassium bromate is not sharp because of formation of the addition compound of quinone with the bromine liberated at the equivalence point. Francis and Hill[19] proposed adding excess of bromate-bromide and determining the unreacted bromate iodometrically. No attempts have previously been made to use indicators for titrating quinol directly with bromate. We have found that DH, BPDM, TFP, PH PCPM and CPH can be used for this purpose. All six give no colour change if the hydrochloric acid concentration is below 0.5*M*; the useful acidity ranges are 0.5–1.5*M* for BPDM and TFP, 0.5–1.0*M* for PH and DH and 0.5–0.8 *M* for PCPM and CPH. At higher acidities the results are too high. The colour change is from light yellow to orange-red in the titration of 0.025–0.05*M* quinol. The end-point colour is stable for about 90 sec. The end-points are brighter and sharper in the titration of 0.0025–0.005*N* quinol. The end-point colour (pink) is stable for about 10 min. At higher acidities under-titration occurs.

BPDM, TFP, PH and DH do not function at sulphuric acid concentrations less than 0.5*M*. CPH does not give a colour change at acidities below 0.25*M* sulphuric acid. BPDM and TFP give sharp end-points in 0.5–1.75*M*, PH in 0.5–0.75*M*, DH in 0.5–1.0*M* and CPH in 0.25–0.4*M* sulphuric acid. Results are too high at higher acidities. The colour change for 0.025–0.05*M* quinol is from light yellow to orange-red which is stable for about 70 sec and the indicator correction is almost negligible. All five indicators give very sharp pink end-points which are stable for about 8 min in the titration of 0.0025–0.005*M* quinol. The results compare favourably with those obtained potentiometrically with cerium(IV) sulphate.

Table 1. Determination of formal potentials (*mV*) of BPDM, TFP, PH, DH, PCPM and CPH

	Potentiopoised method		Schilt's method					
	$[H_2SO_4]M$							
Indicator	0.075	0.20	0.25	0.5	0.75	1.0	1.25	1.50
BPDM	900	—	881	865	838	828	812	793
TFP	—	921	893	881	870	863	854	836
PH	900	—	883	877	870	862	852	842
DH	900	—	856	845	834	825	810	797
PCPM	—	—	807	799	785	771	758	748
CPH	—	—	799	788	760	753	732	721

The minimum potassium bromide concentration required in the titration of 0.025–0.05*M* quinol is ~1.5%, and 1% for titration of 0.0025–0.005*M* quinol. Higher concentrations (up to 16%) do not affect the results.

At least 1.0 ml of 0.2% indicator solution is necessary in the titration of 0.025–0.05*M* quinol but >2.5 ml gives premature end-points. In the titration of 0.0025–0.005*M* quinol 0.5 ml of 0.2% indicator solution is required; >1.5 ml gives higher titration values.

The sharpness of the end-points is in the order BPDM > TFP > DH > PH > CPH > PCPM.

Metol. Metol has not previously been estimated with bromate. Its accurate estimation is of importance because of its application in photography. The methods using iodine,[20] iodine monochloride,[21] cerium(IV) sulphate[9] and sodium vanadate[22] are not quite satisfactory. The estimation with bromate, using DH, BPDM, TFP and PH as reversible redox indicators, is simple but accurate.

Metol is quantitatively oxidized by bromate to *N*-methyl-*p*-quinonimine in a two-electron change in hydrochloric or sulphuric acid medium containing bromide. Stoichiometric results are obtained in sulphuric acid medium ranging from 0.75 to 1.5*M*, with sharp end-point changes from light yellow to an orange-red which is stable for about 70 sec in the titration of 0.025–0.05*M* metol. Low results are obtained at higher acidity and the indicators do not function at lower acidities.

All four indicators give no colour change at acidities less than 0.4*M* hydrochloric acid. BPDM and TFP give sharp colour change from light yellow to orange-red in 0.4–0.8*M* hydrochloric acid and PH and DH in 0.4–0.6*M* hydrochloric acid. The end-point colour is stable for about 90 sec. At higher acidities premature end-points are obtained.

All four indicators give very sharp colour change from very light yellow to pink in the titration of 0.0025–0.005*M* metol. The end-point colour is stable for 2–3 min in hydrochloric or sulphuric acid medium. The indicator correction is almost negligible in the titration of 0.025–0.05 *M* metol. The results compare favourably with potentiometric values

Table 2. Titration of quinol, metol and ascorbic acid in presence of DH, BPDM, TFP, PH, PCPM and CPH indicators

Reductant taken, *mg*	Reductant found,* *mg*	Standard deviation, *mg*
Quinol		
111.3	111.4	0.09
85.5	85.5	0.08
55.4	55.4	0.07
10.43	10.45	0.07
5.58	5.59	0.07
2.23	2.24	0.07
Metol		
157.2	157.3	0.05
120.2	120.2	0.08
40.5	40.5	0.09
15.12	15.14	0.09
12.02	12.04	0.05
4.42	4.43	0.01
Ascorbic acid		
166.3	166.5	0.05
122.4	122.5	0.01
88.5	88.5	0.01
40.6	40.6	0.01

* Average of five determinations.

obtained with cerium(IV) sulphate. The influence of the bromide and indicator concentration is similar to that for titration of quinol.

The sharpness of the end-points is in the order BPDM > PH > TFP > DH.

Ascorbic acid. *p*-Ethoxychrysoidine[2] and 2,6-dichlorophenolindophenol[6] are the only reversible organic indicators recommended for the titration of ascorbic acid with bromate. DH, BPDM, TFP, PH, PCPM and CPH are all suitable as redox indicators in this titration, giving a sharp reversible colour change from colourless to pink (orange-red for TFP). The end-point colour is more stable in hydrochloric than sulphuric acid medium.

BPDM, TFP, PH and DH give no colour change in $<1M$ hydrochloric acid and PCPM and CPH in $<0.5M$ acid. BPDM, TFP and CPH do not function at acidities below $0.75M$ sulphuric acid and PH and DH below $1M$ sulphuric acid. BPDM and TFP give sharp end-points in 1–3M hydrochloric acid, PH and DH in 1–2M hydrochloric or sulphuric acid and BPDM and TFP in 0.75–2.5M and 0.75–2.0M sulphuric acid respectively. CPH gives detectable end-points in 0.5–1M hydrochloric or 0.5–1.75M sulphuric acid and PCPM in 0.5–2M hydrochloric acid. The end-points are brightened and sharpened in the presence of 0.2–1 ml of $10M$ phosphoric acid. The end-point colours of BPDM, TFP, PH, DH and CPH are stable for about 20, 90, 12, 65 and 150 min in hydrochloric acid and 9, 4, 2, 10 and 90 min in sulphuric acid respectively. The end-point colour of PCPM is stable for about 90 sec in hydrochloric acid medium.

The indicator correction is almost negligible. The effect of indicators and bromide concentration is similar to that for quinol. The sharpness of the end-points is in the order TFP > BPDM > DH > PH > CPH > PCPM in hydrochloric acid medium and DH = BPDM > TFP > PH > CPH in sulphuric acid medium.

Oxalic, citric, tartaric, succinic, acetic and malic acids, glucose, fructose, sucrose, starch and acetone do not interfere in the determination of a tenth of their amount of ascorbic acid. The results compare favourably with those obtained by Ballentine.[10]

Comparison with other indicators

All six indicators have advantages over *p*-ethoxychrysoidine in that they give sharper and brighter end-points which can be reversed several times. They are superior to 2,6-dichlorophenolindophenol because (*i*) they give sharper and brighter end-points, (*ii*) the end-point colour is more stable and (*iii*) a slight excess of bromate after the equivalence point does not destroy the colour.

In all the bromate titrations of quinol, metol and ascorbic acid the results are accurate to $\pm 0.2\%$ (Table 2).

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APPLICATION OF SIMPLIFIED COMPLEMENTARY TRISTIMULUS COLORIMETRY TO CHEMICAL KINETICS IN SOLUTION—I

ANALYSIS OF REACTION MIXTURES AND DETERMINATION OF FIRST- OR PSEUDO FIRST-ORDER RATE CONSTANTS

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Summary—A graphical method is described which allows estimation of the number of reacting light-absorbing species from the plots of complementary colour points which are obtained with the use of simplified complementary tristimulus colorimetry (SCTS method) from absorption spectra of a series of kinetic solutions. It is shown that the mole fraction of the reactant or the product at any time can be calculated from the complementary colour points, so that the rate constant can also be determined. The present method has some advantages over the common approach to the determination of reaction rates in presence of a colour impurity.

The number of absorbing species should be accurately known in kinetic studies. Wallace,[1] Ainsworth[2] and others[3–6] have shown that the rank of the matrix of absorbances A_{ij} measured at wavelength i for the jth solution may be taken as equal to the number of absorbing species present in a reaction mixture. However, this method requires the calculation of systematic errors, because it yields as result only the rank of the matrix considered. More recently Coleman, Varga and Mastin[7] have developed a convenient graphical method, which gives the number of absorbing species in solution.

Complementary tristimulus colorimetry (CTS method) has been used as an interesting method for investigation of metal-complex equilibria in solution and for screening of indicators by Reilley,[8,9] Flaschka[10–12] and many other workers.[13–16] By this method each equilibrium species can be located on the complementary colour diagram. The mole fraction of a species in a solution containing two or three components can be calculated from the data on complementary colour points.

In the present paper a simplified CTS (SCTS) method is used for the estimation of the number of reacting species in solution.

Complementary colour points for a series of solutions are also used for the determination of the rate constant of a first or pseudo-first order reaction.

THEORETICAL CONSIDERATIONS

Simplification of CTS method

In the CTS method the absorption spectrum is used to calculate three complementary tristimulus values which define the complementary colour system.[8] For cases when only the changes in concentrations of light-absorbing species are to be studied, it is possible to choose three ranges of wavelengths according to the absorption bands of the species involved, *i.e.*, the ranges u, v and w. The absorbance is measured at regular wavelength intervals within each of these ranges and the sum of absorbances is calculated for each range and used for the calculation of complementary colour points. In kinetic studies, however, the set of absorbance values must be measured rapidly and accurately. Thus in the present work only one absorbance value, measured at a suitable wavelength, is taken to substitute for the sum of absorbances, in each of the three ranges.[17]

The sum of A_u, A_v and A_w is represented by J:

$$J = A_u + A_v + A_w \tag{1}$$

In this case the complementary colour point Q_r corresponding to wavelength r is calculated as

$$Q_r = \frac{A_r}{J} \tag{2}$$

where Q_r becomes Q_u, Q_v and Q_w for $r = u$, v and w, respectively. J is related to the analytical concentration C by

$$J = ECl \tag{3}$$

where l is the light-path length, and E is the overall absorptivity, which is the sum of the molar absorption coefficients for the three wavelengths u, v and w.

Relationship between the number of absorbing species and the colour points

For a system containing k light-absorbing species, the absorbance at wavelength r, A_r, is given by

$$A_r = \sum_{i=1}^{k} c_i \epsilon_{ir} \tag{4}$$

where c_i is the concentration of light-absorbing species i, and ϵ_{ir} is its molar absorption coefficient at wavelength r.

For a series of n solutions and three wavelengths u, v and w, a series of absorbances may be set up as an absorbance matrix, $(A_{s,r})$, *i.e.*,

$$(A_{s,r}) = \begin{pmatrix} A_{1u} & A_{2u} & A_{3u} & \dots & A_{nu} \\ A_{1v} & A_{2v} & A_{3v} & \dots & A_{nv} \\ A_{1w} & A_{2w} & A_{3w} & \dots & A_{nw} \end{pmatrix} \quad (5)$$

In the theory of matrices[18] the rank of the matrix is defined as the order of the largest non-zero determinant which can be obtained from the elements of the matrix, *i.e.*, the rank of equation (5) gives the number of linearly independent elements of the matrix.

In a system of a species R reacting to form a species P, only a single light-absorbing species, either R or P, is present in solution before or after the reaction. In this case the rank of the matrix, which is written for a series of three solutions and three wavelengths u, v and w, is equal to unity, and the determinant (6) must vanish because all its elements are linearly dependent.

$$\begin{vmatrix} A_{1u} & A_{2u} & A_{3u} \\ A_{1v} & A_{2v} & A_{3v} \\ A_{1w} & A_{2w} & A_{3w} \end{vmatrix} = 0 \quad (6)$$

Referred to equations (1) and (2), equation (6) becomes

$$\begin{vmatrix} Q_{1u} & Q_{2u} & Q_{3u} \\ Q_{1v} & Q_{2v} & Q_{3v} \\ 1 & 1 & 1 \end{vmatrix} = 0 \quad (7)$$

Equation (7) states that the points (Q_{1u}, Q_{1v}), (Q_{2u}, Q_{2v}) and (Q_{3u}, Q_{3v}) are found at the same point in the Q_u–Q_v plot[19] for which Q_u and Q_v are co-ordinates of the points. Analogous equations exist for the Q_v–Q_w and Q_w–Q_u plots.

During the reaction of R to yield P, there exist two light-absorbing species in solution and the rank of the matrix is 2: two rows in the determinant (7) are linearly dependent on each other. The result is, in this case, that the three points (Q_{1u}, Q_{1v}), (Q_{2u}, Q_{2v}) and (Q_{3u}, Q_{3v}) fall on a straight line in the Q_u–Q_v plot. Consequently all points for R, P and their mixtures will fall on this system line.

In the course of the consecutive or the competitive reaction denoted by $R \rightarrow P_1 \rightarrow P_2$ or $P_1 \leftarrow R \rightarrow P_2$, there exist three light-absorbing species in solution. Hence, the rank of the matrix is 3, and all elements are linearly independent. Clearly, in this case, the points for R, P_1 and P_2, *i.e.* (Q_{1u}, Q_{1v}), (Q_{2u}, Q_{2v}) and (Q_{3u}, Q_{3v}) respectively, do not fall on a straight line but form a triangle; then, any complementary colour point for a reaction mixture as a function of time should be found in this triangle.

Determination of the rate constant for a first- or pseudo first-order reaction

The rate of a first-order reaction is proportional to the first power of the concentration of only one reactant. This is also true for a pseudo first-order reaction when the reagent is in excess. For this case the rate equation is given by

$$-\ln \frac{[R]_t}{[R]_0} = k_1 \cdot t \quad (8)$$

where $[R]_0$ and $[R]_t$ represent the initial concentration of reactant R and its concentration at any time t, respectively; k_1 is the first- or pseudo first-order rate constant.

In the SCTS method the absorbance at wavelength u for a solution at any time t is given by

$$A_{tu} = \epsilon_{Ru}[R]_t + \epsilon_{Pu}[P]_t \quad (9)$$

where $[P]_t$ is the concentration of the product P at any time t. By division of both sides by $([R]_t + [P]_t)$ and substitution of the mole fraction q defined by

$$q = \frac{[R]_t}{[R]_t + [P]_t} \quad (10)$$

equation (9) becomes

$$\frac{A_{tu}}{[R]_t + [P]_t} = q \cdot \epsilon_{Ru} + (1 - q) \cdot \epsilon_{pu} \quad (11)$$

Analogous equations can be derived for A_{tv} and A_{tw}; from equation (1) the following equation can be given:

$$\frac{J}{[R]_t + [P]_t} = q \cdot E_R + (1 - q) \cdot E_P \quad (12)$$

where E_R and E_P are the overall absorptivities of the reactant and the product, which can be evaluated by using equation (3).

The two absorbances for the reactant and the product at any time are given at wavelength u by

$$A_{R,tu} = \epsilon_{Ru} \cdot [R]_t \quad (13)$$

$$A_{P,tu} = \epsilon_{Pu} \cdot [P]_t \quad (14)$$

Thus the complementary colour points for wavelength u of the reactant and the product are given at any time t by the following expressions obtained by combining equations (2), (3), (13) and (14).

$$Q_{R,tu} = \frac{A_{R,tu}}{E_R \cdot [R]_t} = \frac{\epsilon_{Ru}}{E_R} \quad (15)$$

$$Q_{P,tu} = \frac{A_{P,tu}}{E_P \cdot [P]_t} = \frac{\epsilon_{Pu}}{E_P} \quad (16)$$

By substituting equations (15) and (16) into equation (11), and considering that the complementary colour points of both the reactant and the product are independent of time, the following equation is obtained:

$$\frac{A_{tu}}{[R]_t + [P]_t} = q \cdot Q_{Ru} \cdot E_R + (1 - q) \cdot Q_{Pu} \cdot E_P \quad (17)$$

Substitution of equations (2) and (12) into equation

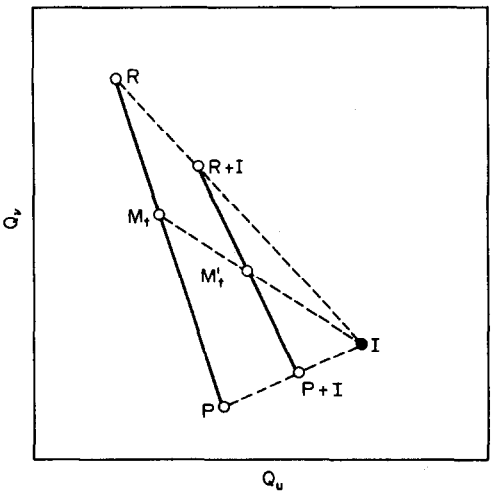

Fig. 1. Q_u–Q_v plot for a reaction of the reactant R forming the product P in the presence of a non-reactive light-absorbing species. Complementary colour points: R: reactant; P: product; I: non-reactive light-absorbing species; R + I: mixture of R and I; P + I: mixture of P and I; M_t: reaction mixture of R and P at any time; M'_t: reaction mixture of R, P and I at same time.

(17) yields the relationship between the mole fraction and the complementary colour points at wavelength u,

$$q = \frac{E_P \cdot (Q_{Pu} - Q_{tu})}{E_R \cdot (Q_{tu} - Q_{Ru}) + E_P \cdot (Q_{Pu} - Q_{tu})} \quad (18)$$

Analogous equations for the mole fraction can also be obtained for wavelengths v and w.

Since $[R]_0 = [R]_t + [P]_t$, the rate equation (8) can be written in terms of the mole fraction, q, [*cf.* equation (10)] as

$$-\ln q = k_1 \cdot t \quad (19)$$

Thus the values of q can be calculated from the complementary colour points by equation (18) and expressed as a function of time.

When the reactant R reacts to form the product P in the presence of an absorbing species, I, which does not take part in the reaction, a series of complementary colour points will be displaced from the original system line connecting the colour points of the reactant and the product and will fall on a new straight line connecting the colour points of the mixtures of R and I, and P and I. The Q_u–Q_v plot for this case is illustrated in Fig. 1. The mole fraction at any time is calculated from the complementary colour parameters of mixtures by using equation (18), and the rate constant can be determined similarly by equation (19).

EXPERIMENTAL

Reagents

All solutions of dyes in ethanol were prepared from commercial reagents and were not recrystallized before use. All other reagents used were of guaranteed reagent grade, and distilled water was used to make up solutions.

Apparatus

Measurements of absorbances and calculations of complementary colour points were made on a Shimadzu Model UV-200 Spectrophotometer with a Shimadzu Model WP-1 Wavelength-programmer, a Shimadzu Model DM-2 Digitalmeter, a Shimadzu Model CIF-1 Interface and a Seiko Model S-301S Calculator. The temperature of the cell compartment was controlled within $\pm 0.1°$ by a Sharp Model TE-10K Thermoelectric circulating bath. Measurements of pH were made with a Hitachi-Horiba Model F-7 pH-meter.

Procedure

All the procedures were as described in the literature.[20,21,24,25]

RESULTS AND DISCUSSION

Analysis of the number of absorbing species in reaction mixtures

The reaction between permanganate ions and oxalic acid. The reaction between permanganate ions and oxalic acid has been studied by many workers as an example of an intermediate complex compound. Manganese(III) forms a yellow dioxalate complex, $Mn(C_2O_4)_2^-$, and a cherry-red trioxalate complex, $Mn(C_2O_4)_3^{3-}$.[22] In aqueous solution they are easily converted one into the other, according to the reversible reaction

$$Mn(C_2O_4)_3^{3-} + 2H_2O \rightleftharpoons Mn(C_2O_4)_2 \cdot (H_2O)_2^- + C_2O_4^{2-} \quad (20)$$

When the initial solution contains enough manganous and oxalate ions, the reaction involves two processes:

$$MnO_4^- + 4Mn^{2+} + 5mC_2O_4^{2-} + 8H^+ \rightarrow 5Mn(C_2O_4)_m^{3-2m} + 4H_2O \quad (21)$$

$$2Mn(C_2O_4)_m^{3-2m} \rightarrow 2Mn^{2+} + (2m-1)C_2O_4^{2-} + 2CO_2 \quad (22)$$

Process (21) takes place almost instantaneously and is followed by the subsequent slower process (22). Cartledge and Ericks[23] have shown that a cherry-red trioxalate complex exists only at high pH. Hence, it must be assumed that only the yellow dioxalate complex exists in a hydrochloric acid solution initially containing enough manganous ions and oxalic acid, and that it disproportionates with time. The complementary colour points given in Table 1 suggest that only one complex exists. Figure 2 shows the absorption spectra of the solution containing manganous and oxalate ions at a relatively high pH. This solution contains both the yellow dioxalate complex and the cherry-red trioxalate complex, each complex undergoing decomposition. The Q_u–Q_v plot for this system is presented in Fig. 3. Permanganate does not react directly with oxalate and so during the first reaction period potassium permanganate exists in solution, which is shown by the fact that the complementary colour points do not fall on the system line connecting points for mixtures of the dioxalate and the trioxalate complexes.

Table 1. The change in Q_t for a solution of $KMnO_4$ containing sufficient initial manganese(II) and oxalic acid in 0.4*M* hydrochloric acid*

Reaction time, (*min*)	Q_{tu} (490 nm)	Q_{tv} (400 nm)	Q_{tw} (355 nm)
1.00	0.262	0.142	0.596
2.25	0.270	0.162	0.568
3.50	0.267	0.152	0.581
4.75	0.270	0.145	0.586
6.00	0.280	0.180	0.540
	Av. 0.270	Av. 0.156	Av. 0.574

* $1.62 \times 10^{-3}M$ $KMnO_4$, $4.00 \times 10^{-2}M$ oxalic acid, $6.50 \times 10^{-3}M$ $MnCl_2$ and 0.4*M* HCl.

The catalytic decomposition of hydrogen peroxide by mixed catalysis. Uri[24] has determined the overall reaction rate of the catalytic decomposition of hydrogen peroxide by sodium tungstate in the presence of copper(II). The reaction mechanism is:

$$Cu^{2+} + HWO_6^- \rightleftharpoons Cu^+ + HWO_6^{\cdot} \quad (23)$$

$$\ulcorner \rightarrow HWO_6^{\cdot} + H_2O_2 \rightarrow HWO_5^{\cdot} + H_2O + O_2\uparrow \quad (24)$$

$$\llcorner\ HWO_5^{\cdot} + H_2O_2 \rightarrow H_2O + HWO_6^{\cdot} \quad (25)$$

(the pertungstate is formed when hydrogen peroxide is mixed with tungstate).

The absorption spectra were thus obtained for the decomposition of a blue copper(II) citrate complex and the formation of a green copper(I) citrate complex of stoichiometry 1:1; the Q_w–Q_u plot is presented in Fig. 4. Since there are two absorbing species during the reaction, a straight line is obtained.

The oxidation of sulphonephthalein dyes by periodate. Ellis and Mottola[25] have studied the oxidation reaction of sulphonephthalein dyes by periodate, catalysed by manganese in basic media. Cresol Red (*o*-cresolsulphonephthalein) and Cresol Purple (*m*-cresolsulphonephthalein) react with manganese oxidized to a higher oxidation state by trihydrogen orthoperiodate, $H_3IO_6^{2-}$, and produce the corresponding oxidized compounds. Figure 5 shows a Q_u–Q_v plot for the processes of oxidation of Cresol Red and Cresol Purple by periodate. Straight lines were obtained in both cases. In Fig. 6 a Q_u–Q_v plot illustrates the oxidation of a mixture of Cresol Red and Cresol Purple. Both dyes react competitively, so the complementary colour points are located within the triangle formed by the colour points of Cresol Red, Cresol Purple and the reaction product.

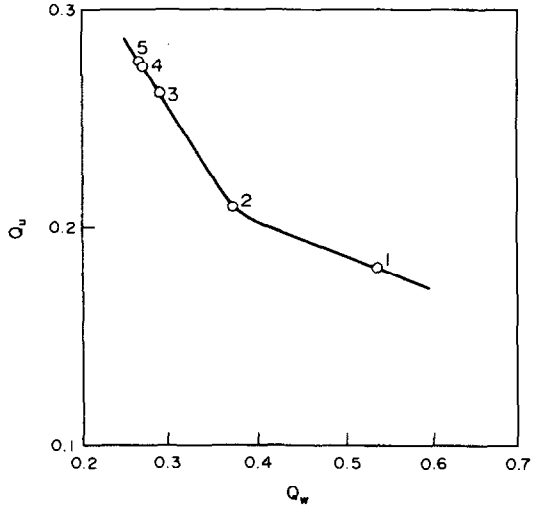

Fig. 3. Q_w–Q_u plot for reaction mixtures containing manganese(II) and oxalate ions. The following wavelengths were chosen; *u*: 500 nm; *v*: 440 nm; *w*: 370 nm. Reaction times (*min*); 1: 0.67; 2: 1.83; 3: 3.00; 4: 4.17; 5: 5.50.

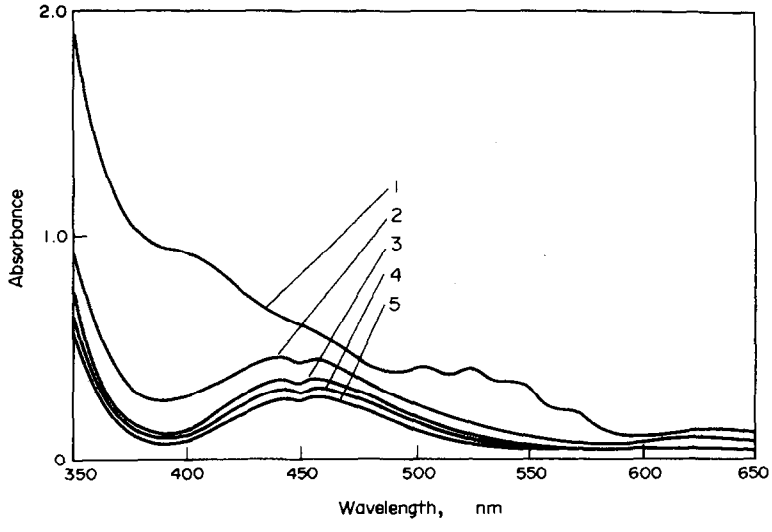

Fig. 2. Absorbance curves for solutions of potassium permanganate containing manganese(II) and oxalate ions. Solutions were $1.62 \times 10^{-3}M$ in $KMnO_4$, $2.00 \times 10^{-2}M$ in oxalic acid and $8.12 \times 10^{-4}M$ in $MnCl_2$. Reaction times (*min*): 1: 0.67; 2: 1.83; 3: 3.00; 4: 4.17; 5: 5.50.

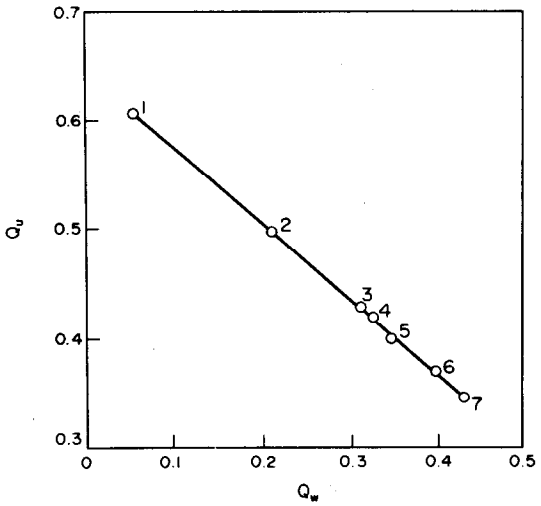

Fig. 4. Q_w–Q_u plot for reaction mixtures of hydrogen peroxide and tungstate in which the blue copper(II) citrate complex is converted into the green copper(I) citrate complex. The concentrations in the initial solution were $4.00 \times 10^{-2}M$ Na_2WO_4, $4.02 \times 10^{-2}M$ $Cu(NO_3)_2$, $0.04M$ sodium citrate, $0.08M$ H_2O_2 and $0.08M$ CH_3COOH. The following wavelengths were chosen: *u*: 690 nm; *v*: 640 nm; *w*: 410 nm. Reaction times (*min*): 1: 0; 2: 1.00; 3: 3.00; 4: 5.00; 5: 7.00; 6: 9.00; 7: ∞.

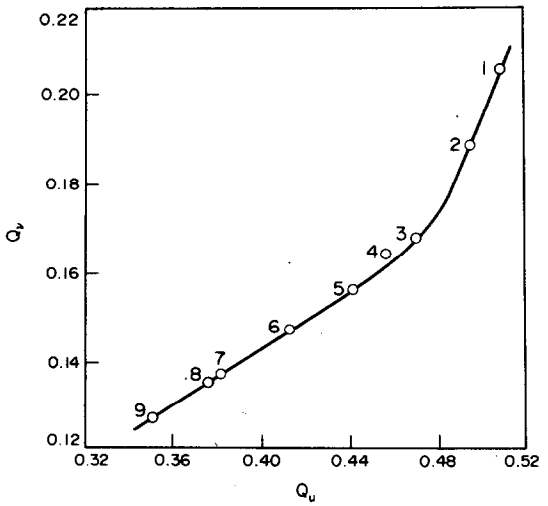

Fig. 6. Q_u–Q_v plot for oxidation of Cresol Red and Cresol Purple mixture with manganese(II) as catalyst. The following wavelengths were chosen: *u*: 575 nm; *v*: 530 nm; *w*: 380 nm. Concentrations of dye mixture: $1.20 \times 10^{-5}M$ Cresol Red and $0.20 \times 10^{-5}M$ Cresol Purple. Concentrations of reagents: $2.0 \times 10^{-3}M$ KIO_4 and $1.0 \times 10^{-4}M$ $MnCl_2$. Reaction times (*min*): 1: 4.5; 2: 6.0; 3: 10.5; 4: 14.0; 5: 16.0; 6: 18.0; 7: 24.0; 8: 26.0; 9: 30.0.

Determination of pseudo first-order rate constants from the complementary colour points

A series of solutions $1.0–1.5 \times 10^{-5}M$ in Cresol Red was prepared and the complementary colour points for the oxidation process were calculated as given above. Table 2 lists the complementary colour points as a function of time, the initial colour points, the final colour points and the overall absorptivities.

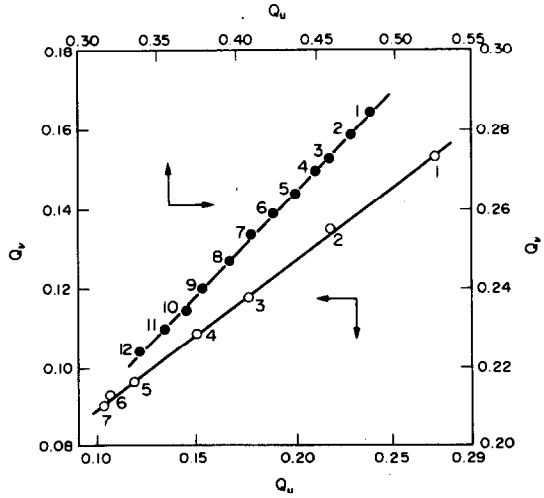

Fig. 5. Q_u–Q_v plot for oxidation of Cresol Red and Cresol Purple by periodate in presence of manganese(II) as catalyst. —O—O—: Cresol Red ($10^{-5}M$), *u*: 575 nm; *v*: 530 nm; *w*: 400 nm. Reaction times (*min*): 1: 3.0; 2: 4.0; 3: 5.0; 4: 6.0; 5: 7.0; 6: 8.0; 7: 9.0. —●—●—: Cresol Purple ($10^{-5}M$), *u*: 570 nm; *v*: 527 nm; *w*: 420 nm. Reaction times (*min*): 1: 6.0; 2: 8.0; 3: 10.0; 4: 11.0; 5: 13.0; 6: 14.0; 7: 15.0; 8: 19.0; 9: 23.0; 10: 26.0; 11: 27.0; 12: 30.0. Concentrations of reagents: $2.0 \times 10^{-3}M$ KIO_4 and $1.0 \times 10^{-4}M$ $MnCl_2$.

The reaction was completed after about 20 min. Ellis and Mottola[25] have found that this oxidation is a pseudo first-order reaction under given conditions. The mole fractions were calculated from equation (18) as a function of time for each of the three wavelengths with the use of the values in Table 3, and the rate constants were determined by equation (19). In kinetic runs it is usually difficult to know when the reaction has gone to completion. In an SCTS plot, when two or more points coincide, their position can be taken as the final point for the calculation of the mole fraction.

For Cresol Purple the measurements were carried out in the same manner, and the pseudo first-order rate constant was determined from the complementary colour parameters. As can be seen from the results listed later, in Table 4, the rate constant of Cresol Purple has a different value for the three wavelengths. The absorbance maximum of Cresol Purple is at 580 nm under the conditions used, and the wavelength selected for *u* is 575 nm. It is assumed, therefore, that the value of the rate constant for the wavelength *u* is the correct one.

The value of the pseudo first-order rate constant for Bromocresol Green has been reported by Ellis *et al.* to be 0.042×10^{-2} min^{-1} under given conditions. During a 10-min interval, only Cresol Red may be considered to react, as Bromocresol Green reacts so slowly that it does not interfere appreciably. It is easy to determine the rate constant of Cresol Red in the presence of Bromocresol Green by the SCTS method. A series of solutions, $1.524 \times 10^{-5}M$ in Cresol Red and $0.502 \times 10^{-5}M$ in Bromocresol Green, was taken for the measurements. In this case the in-

Table 2. The change in Q_r during oxidation of Cresol Red, and the values Q_r, E for the reactant and the product*

Reaction time, (*min*)	Q_{tu} (575 nm)	Q_{tv} (530 nm)	Q_{tw} (400 nm)	
1.00	0.449	0.210	0.341	
2.00	0.345	0.180	0.475	
3.00	0.270	0.154	0.576	
4.00	0.209	—	0.654	
5.00	—	0.115	0.718	
Reactant† ($t = 0$)	Q_{Ru} (575 nm)	Q_{Rv} (530 nm)	Q_{Rw} (400 nm)	E_R
	0.596	0.268	0.135	6.03×10^4
Product‡ ($t = \infty$)	Q_{Pu} (575 nm)	Q_{Pv} (530 nm)	Q_{Pw} (400 nm)	E_P
	0.076	0.085	0.827	2.13×10^4

* Reagents: $2.0 \times 10^{-3} M$ KIO_4 and $1.0 \times 10^{-4} M$ $MnCl_2$.
† Cresol Red concentrations: $1.00–1.50 \times 10^{-5} M$.
‡ These values were calculated from the absorbances of the reaction mixture after 20 min.

Table 3. The change in Q_r during oxidation of Cresol Red in the presence of Bromocresol Green, and the values Q_r, E for the reactant and the product*

Reaction time, (*min*)	Q_{tu} (620 nm)	Q_{tv} (575 nm)	Q_{tw} (400 nm)	
1.00	—	—	0.233	
2.50	0.382	—	0.281	
4.00	—	0.302	—	
5.50	0.404	0.291	—	
7.00	0.408	—	—	
8.50	0.410	—	—	
Reactant† ($t = 0$)	Q_{Ru} (620 nm)	Q_{Rv} (575 nm)	Q_{Rw} (400 nm)	E_R
	0.214	0.696	0.089	6.37×10^4
Product‡ ($t = \infty$)	Q_{Pu} (620 nm)	Q_{Pv} (575 nm)	Q_{Pw} (400 nm)	E_P
	0.412	0.210	0.378	3.08×10^4

* Reagents: $2.0 \times 10^{-3} M$ KIO_4 and $1.0 \times 10^{-4} M$ $MnCl_2$.
† Dye mixture: Cresol Red $1.524 \times 10^{-5} M$ and Bromocresol Green $0.502 \times 10^{-5} M$.
‡ These values were calculated from the absorbances of the reaction mixture containing Bromocresol Green after 10 min.

Table 4. Pseudo first-order rate constants, k_1 (min^{-1})*, of Cresol Red and Cresol Purple, and Cresol Red in the presence of Bromocresol Green†

Wavelength	Cresol Red	Cresol Purple‡	Wavelength	Cresol Red containing Bromocresol Green
u (575 nm)	48.2	7.46	u (620 nm)	48.9
v (530 nm)	46.3	3.85	v (575 nm)	46.9
w (400 nm)	49.7	6.50	w (400 nm)	34.1

* Mean value of five determinations.
† All experiments were carried out at pH 9.0 (Clark–Lubs buffer), $\mu = 0.1$ (KCl) and temperature $28 \pm 0.1°$.
‡ The three wavelengths for Cresol Purple were the same as those for Cresol Red.

itial colour points for the three wavelengths and the overall absorptivity were calculated from the absorbance values of the mixture of Cresol Red and Bromocresol Green by using the particular concentration of each indicator. The final parameters were calculated from one of the reaction solutions containing the product of Cresol Red and unreacted Bromocresol Green after 10 min. The results are summarized in Table 3. With the use of these values, the pseudo first-order rate constants of Cresol Red in the presence of Bromocresol Green were determined from equations (18) and (19) (see Table 4).

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SHORT COMMUNICATIONS

PRECIPITATION OF ZINC AMMONIUM PHOSPHATE FROM HOMOGENEOUS SOLUTION*

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Summary—Urea hydrolysis has been employed to raise the pH for homogeneous precipitation of zinc ammonium phosphate. From 30 to 100 mg of zinc can conveniently be determined by this technique (relative standard deviation 0.2% for 89 mg). The interference of nickel was minimized by using ammonium tartrate as masking agent, but copper could not be effectively masked with the same tartrate. Ammonium tartrate obtained from a different source was found to mask the copper more effectively. Investigations showed that the latter tartrate contained an appreciable amount of ammonium oxalate.

Zinc has been precipitated as sulphide from homogeneous solution by the hydrolysis of thioacetamide,[1–4] thiourea[5] and trithiocarbonic acid,[6–8] but the determination requires conversion of the ZnS into ZnO at 1000° or use of a suitable titrimetric method. Precipitation of zinc 8-quinolinolate and quinaldinate has been reported by various workers.[9–12] Doubts have been expressed about the drying temperature for zinc oxinate and hence the final determination is often completed titrimetrically. Zinc oxalate has been precipitated from homogeneous solution and the determination completed titrimetrically with permanganate.[13] None of these methods can be applied for the determination of zinc in presence of copper and nickel without preliminary separation. Precipitation of zinc ammonium phosphate, by either cation or anion release techniques,[14,15] has not been applied to its separation from copper and nickel, which is the subject of the present paper.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical-grade chemicals unless otherwise specified.

Zinc solution, 0.05M. Prepared by dissolving granulated zinc in hydrochloric acid and diluting; standardized by a conventional procedure.[16]

Ammonium dihydrogen phosphate solution, 10%.

Ammonium tartrate. Sample A: ammonium tartrate C.P. supplied by FOCH, Gliwice. Poland. Sample B: ammonium (+)-tartrate, AnalaR, supplied by BDH, India.

Wash solutions. (*a*) Diammonium hydrogen phosphate solution, 1%, was adjusted to pH 6.8. (*b*) Neutral aqueous ethyl alcohol (50% v/v).

Procedure

To 25 ml of solution, containing 30–100 mg of zinc, add 10 g of ammonium chloride or sulphate, 10 ml of 10% ammonium dihydrogen phosphate solution and 20 g of urea, dilute to 200 ml with distilled water and place a boiling stick in the solution to avoid bumping. Cover with a watch-glass and keep the beaker for about 6 hr in an oven at 95–100°. Add distilled water occasionally to compensate for the water lost by evaporation. Cool, filter off the precipitate on a weighed porosity-3 sintered-glass crucible and wash it with wash solution (*a*) until free from chloride and sulphate and then with wash solution (*b*) until free from phosphate. Dry at 105–110° to constant weight.

RESULTS AND DISCUSSION

The precipitate settled readily as soon as it formed and appeared coarse and crystalline, unlike the precipitate (a fine powder) obtained by the conventional procedure. The relative particle sizes of the precipitates obtained by the conventional and the homogeneous solution procedures were measured by microscope and by heterogeneous isotopic-exchange[17] with ^{65}Zn. By the microscopic method, the particles obtained by PFHS were found to be about 5 times as big as those obtained by conventional procedure, and the isotopic-exchange method showed the surface area of the particles obtained by the conventional method to be about 7 times that of the particles obtained by PFHS. The determination

* Presented at the Annual Convention of Chemists, Jaipur (India) 1977.

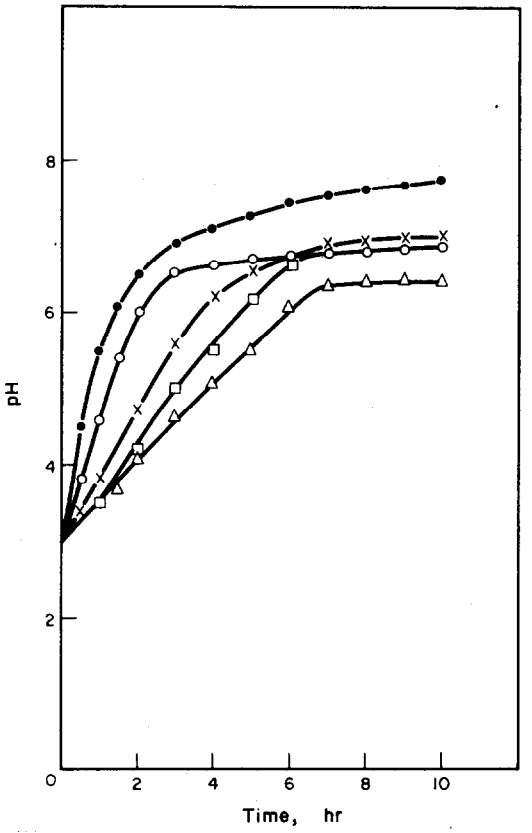

Fig. 1. Increase in pH with time in presence of various anions: —●— without any buffer; —○— ammonium chloride; —×— ammonium sulphate; —△— ammonium acetate or ammonium succinate; —□— ammonium tartrate.

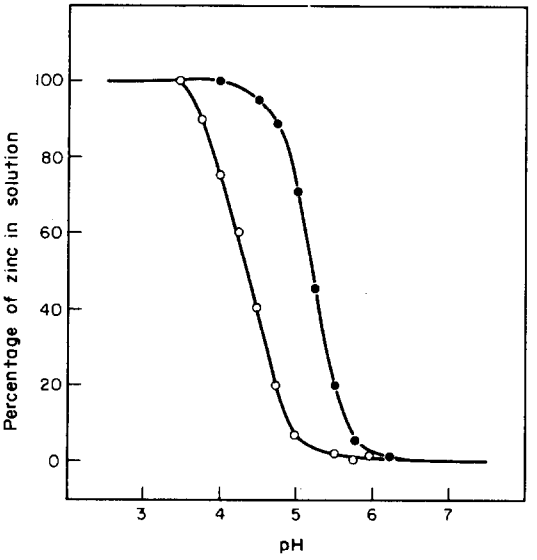

Fig. 2. Zinc left in solution (determined by EDTA titration), as a function of pH: —○— by direct addition of ammonia solution and also by PFHS in presence of ammonium chloride, ammonium sulphate, ammonium acetate or ammonium succinate; —●— by PFHS in presence of ammonium tartrate.

was quantitative and for 10 determinations of 89.4 mg of zinc, the maximum deviation and standard deviation found were 0.2 mg and 0.15 mg respectively. The error was within ±0.5% for a solution containing 30–100 mg of zinc.

Effect of anions

Figure 1 shows the increase in pH with time in presence of 5 g of buffer, 1 g of ammonium dihydrogen phosphate and about 80 mg of zinc per 100 ml of solution, and Fig. 2 shows the fraction of zinc left in solution, as a function of pH. The increase in pH is slow in presence of ammonium salts of organic acids (Fig. 1) and precipitation is delayed in presence of tartrate (Fig. 2). The precipitation does not take place at all in the presence of citrate. The precipitate obtained in the presence of salts of organic acids was in the form of thin shining sheets, whereas dense needles were obtained in the presence of inorganic salts. The change in crystal shape may be due to buffer action,[18] complex formation[19] or incorporation of organic ions in the precipitate. However, no organic anions could be detected analytically in the precipitates.

Effect of cations

The following surprising observations were made when ammonium tartrates obtained from different sources were employed. It was found that tartrate supplied by FOCH, Poland (sample A) minimized the co-precipitation of copper more effectively than did that obtained from BDH, India. The reverse was the case for nickel. When sample B was employed for Cu(II), zinc could be determined within ±1% error in the presence of 40 mg or less of copper whereas with sample A as much as 300 mg of Cu(II) could be masked. On the other hand, when sample A was employed for Ni(II), the entire contents of the beaker were found to be colloidal and greenish in colour and this reagent could not be used; sample B could be safely used for up to 300 mg of nickel(II). The precipitate obtained within 6 hr was found to be contaminated with copper and nickel, but when the digestion at 95–100° was continued for about 10 hr, no contamination was observed. The results for determination of zinc in presence of different amounts of samples A and B are given in Table 1. It was observed that the contamination decreased with increase in ammonium tartrate concentration, but when the amount used exceeded 25 g, the precipitate obtained was colloidal and sticking to the walls of the beaker. This effect was even more pronounced in conventional precipitation.

The tartrate complexes of copper with both samples were prepared under identical conditions and they were analysed for copper content after decomposition. It was found that the complex made with sample A contained 31.3% copper and that with sample B only 18.8%. Polarograms were taken for copper in the two tartrate solutions and it was found that the half-wave potential with sample A was more negative than that with sample B for the same con-

Table 1. Effect of copper and nickel on determination of 89.4 mg of zinc

Foreign ion added, mg	Zinc found, mg
Ni 40*	89.2, 89.3
60	89.9, 89.9
80	91.3, 91.3
100	91.4, 91.5
200†	89.5, 89.4
Cu 100§	89.4, 89.4
140	89.8, 89.8
180	90.1, 90.1
200‡	89.1, 89.1
20*	90.2, 90.2
40	90.4, 90.3
60	90.4, 90.4
80†	90.5, 90.4

* 5 g of ammonium tartrate, sample B added.
† 10 g of ammonium tartrate, sample B added.
§ 5 g of ammonium tartrate, sample A added.
‡ 10 g of ammonium tartrate, sample A added.

centration of metal and tartrate. This was considered to be due to the presence of impurity in one of the samples. Optical rotation measurements, solubility tests and microanalysis proved that sample A was contaminated. Attempts were therefore made to isolate the impurity on the basis of the difference in the solubilities in water (A 28.5 g/100 ml; B 46.8 g/100 ml at 25°) and then identify it. The impurity was isolated, recrystallized, and identified as ammonium oxalate by qualitative analysis, microanalysis and infrared spectroscopy. From the optical rotation measurements, the Polish material appeared to be only about 90% pure.

It is well known that zinc precipitates quantitatively when treated with ammonium oxalate. Under the experimental conditions described above, the precipitation of zinc did not take place in the presence of ammonium tartrate, presumably because of complex formation. It was found that 300 mg of copper could be effectively masked by addition of a mixture of 10 g of ammonium tartrate and 1–3 g of ammonium oxalate (Table 2). In presence of 300 mg of nickel, the determination could not be done when the amount of oxalate in the mixture exceeded 400 mg. With 100 mg or less of nickel(II) present, higher amounts of oxalate (up to 1 g) could be tolerated. Attempts were made to precipitate zinc in presence of 200 mg each of copper and nickel, when present together. When more than 600 mg of ammonium oxalate was added, the precipitate was found to contain nickel, and when less than 1 g was added the precipitate was contaminated with copper. However, zinc could be determined within ±1% error, in presence of 300 mg of copper and 100 mg of nickel, by using a mixture of 15 g of ammonium tartrate and 500 mg of ammonium oxalate.

Table 3. Comparison between PFHS and conventional procedures (89.4 mg of zinc)

Ammonium tartrate added, g	Foreign ion added, mg	Amount of zinc found, mean value of three determinations, mg	
		PFHS	Conventional
15 (Sample A)	Cu 320	89.5	92.5
15 (Sample B)	Ni 320	89.4	92.6

Table 3 shows the superiority of the PFHS method.

It was also observed that small amounts of iron(III) could be masked with 10 g of ammonium tartrate plus 2 g of ammonium oxalate. However, the precipitate was slightly yellow, showing the presence of iron(III). Presence of 300 mg of sodium or potassium did not interfere in the procedure provided the precipitation was conducted in the presence of excess of ammonium salts; otherwise potassium interfered.

A brass sample was analysed for zinc after separation of tin and lead. A mixture of 10 g of ammonium tartrate and 1 g of ammonium oxalate was used as masking agent. The proposed method gave a value of 31.3 ± 0.05% whereas the standard procedure[20] gave a value of 31.4 ± 0.21%.

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Table 2. Effect of oxalate + tartrate in masking copper and nickel in determination of 89.4 mg of zinc

Foreign ion added, mg	Amount of masking agent	Zinc found, mg	Difference, mg
Ni 200	15 g of tartrate + 1 g of oxalate	94.4, 94.7	+5.0, +5.3
100	15 g of tartrate + 1 g of oxalate	90.3, 90.2	+0.9, +0.8
200	15 g of tartrate + 400 mg of oxalate	89.6, 89.6	+0.2, +0.2
Cu 300	10 g of tartrate + 500 mg of oxalate	89.8, 89.8	+0.4, +0.4
300	10 g of tartrate + 1 g of oxalate	89.3, 89.3	−0.1, +0.1
Cu 300, Ni 100	15 g of tartrate, 500 g of oxalate	89.5, 89.5	+0.1, +0.1

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A CONTINUUM-SOURCE SINGLE-DETECTOR RESONANCE-MONOCHROMATOR FOR ATOMIC-ABSORPTION SPECTROMETRY†

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Summary—The detector, for atomic-absorption spectrometry, consists of a furnace into which a constant concentration of the element to be analysed is atomized. Resonance radiation is excited by the light from a xenon-arc lamp which traverses the burner flame. The resonance radiation passes through a tunable grating filter and is measured with a photomultiplier.

Resonance monochromators for atomic-absorption spectrometry (AAS) have been an attractive proposition since Russell and Walsh[1] observed resonance radiation from a hollow-cathode lamp in 1959. Experimental use of resonance monochromators as detectors for AAS has centred around the use of specific atomic-line sources (electrodeless discharge lamps, EDLs; and hollow-cathode lamps, HCLs), and individual element-sputtering, thermal, or flame atom-cloud generators.[2–4] The present work involves the use of a continuum source and an atmospheric-pressure flow-through Molnar and Winefordner type[5] furnace for atom generation. Preliminary detection limits for Cu and Mg are included as well as a discussion of sensitivity.

The advantages realized by use of a resonance monochromator as a detector for AAS are manifold. They include simplicity of design, ease of use, right-angle geometry and elimination of the monochromator generally used to isolate the line of interest. These advantages were realized in a commercial instrument in the late 1960s. The major reason for the lack of acceptance of this instrument was the necessity to use a different source and detector for each element, thus incurring quite a large expense for routine operation.

The present work concentrates on the use of a single-source, single-detector system, with an inexpensive tunable grating filter (low-resolution, large aperture). The basis for the continuum-source resonance detector is evident from the plot of log I_F (atomic-fluorescence intensity) *vs.* log analyte concentration (Fig. 1), which exhibits a plateau, as predicted by Hooymayers[6] and by Winefordner *et al.*[7] The plateau region of this curve should result in freedom from the low-frequency noise produced in the nebulization–atomization process. Changes in the analyte concentration produced by fluctuating gas flows and flame conditions should result in no I_F fluctuation, because the derivative of I_F with respect to the analyte concentration is zero, making the signal limited by analyte shot noise (or by background flicker noise in a few cases).

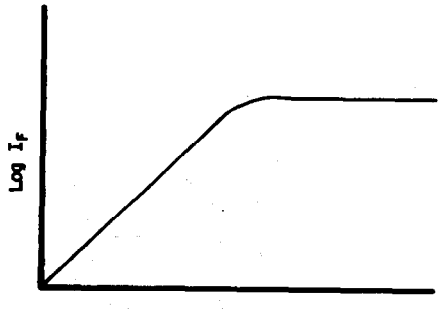

Fig. 1. Log atomic-fluorescence intensity *vs.* log analyte concentration.

EXPERIMENTAL

To realize the advantages of the resonance monochromator, the design of the atom cell must be carefully considered. The most important characteristics are high temperature and an inert or reducing atmosphere to produce good atomization of a wide range of analyte species, and low background to yield low emission noise.

Molnar and Winefordner's furnace design[5] provides these advantages and was used with minor modifications. The furnace power-supply used provides an operating temperature of 2100° (measured by optical pyrometer) at a power dissipation of 1.9 kW. The flow-gas is argon, with enough hydrogen to support a diffusion flame. A low flow-rate of methane is used to provide longer carbon-furnace tube-life.

System design (Fig. 2) included the following considerations. The source was chosen for output power, with reasonable stability. Standard optics for atomic fluorescence were chosen, with the exception of a collimated section for the atomic-absorption flame. A slit mask immediately followed the second lens to provide some semblance of the geometry of the three-slot burner used with a standard Perkin-Elmer chamber for the AA measurements. Collection of the resonance radiation is through one lens to a 0.1-m tunable grating filter (monochromator) with a 40-Å bandpass; the grating filter is used to reduce the amount of stray room-light striking the photomultiplier and to minimize background and scatter.

The detector is supplied with desolvated salt particles at a low gas flow-rate by an ultrasonic nebulizer system, providing a residence time consistent with the detector requirements.

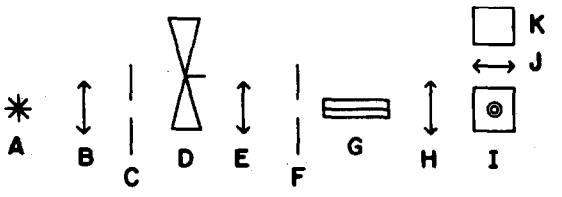

Fig. 2. Experimental system: A, 300-W Eimac continuum Xe lamp; B, focusing lens; C, iris diaphragm; D, chopper; E, collimating lens; F, slit mask; G, 3-slot burner; H, focusing lens; I, flow-through furnace; J, collection lens; K, tunable grating filter.

Table 1. Furnace operating characteristics

Gas flow-rates, *l./min*	Ar 0.43
	H_2 1.10
	CH_4 0.083
Power 1.9 kW (235 A at ~8 V)	
Temperature 2100°C	
Residence time 4 msec	

The furnace operating characteristics are given in Table 1. All measurements are made under the same furnace atom-cell conditions. The furnace tubes are high-temperature graphite precoated with a layer of pyrolytic graphite as described by Clyburn *et al.*[8] The operating temperature should be kept high in order to maintain the pyrolytic coating, thereby increasing tube-life.

RESULTS

Preliminary high detection limits of 0.1 ppm for both Cu and Mg indicated a problem with system noise. This was traced to two sources, a faulty regulation card in the lamp power-supply causing major noise problems in the detector output, and flame wander in the furnace. Use of the 900-W xenon short-arc lamp eliminated much of the lamp noise. (Unfortunately, the power supply failed before significant experimentation could be completed.) Preliminary experiments with a quartz sheath have shown the possibility of reduction in flame-wander noise. In addition, a new furnace has been built to give isokinetic sheathing.

A sensitivity for copper (IUPAC characteristic concentration) of 0.27 μg/ml was somewhat less than that of line-source atomic-absorption measurements. It should have been of the order of Cochran and Hieftje's result from droplet modulation AAS, 0.073 μg/ml,[9] but was about four times higher. A possible explanation is that the increased line-width due to operation on the plateau of Fig. 1 caused the sensitivity loss. However, the sensitivity was better than that indicated by Cochran and Hieftje for conventional AAS with a continuum source (0.66 μg/ml).

Several extensions are possible for a system of the type described, *e.g.*, simultaneous multielement AAS by use of either interference filters or a direct reader system. Magnesium was measured with a filter-type system and a comparable detection limit was obtained. For simultaneous analysis, a multielement mixture would be introduced into the atom cell, producing resonance radiation at the characteristic wavelength of each element. An experiment of this type has led to usable resonance signals for Cu, Ca, Mg, Cr and Ni, observed by scanning the spectrum, while keeping all atomization conditions the same as listed in Table 1. Other possible uses of the present system include isotope detection, and determination of elements for which HCLs or EDLs give poor performance.

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ACCURATE DETERMINATION OF SULPHUR IN STEELS AND CERTAIN HEAT-RESISTING ALLOYS BY ISOTOPE DILUTION MASS SPECTROMETRY

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Summary—A mass spectrometric isotope dilution method for the determination of sulphur in steels and certain alloys has been investigated. Addition of bromine in the dissolution of carbon steels was necessary for the complete conversion of sulphur into sulphate. The relative standard deviation was better than 1.5% for sulphur contents in the range 40–3,000 ppm. The results on standard materials were in good agreement with the certified values for samples of BCS, but lower than those for JSS and NBS.

Although the rapid combustion method for the determination of sulphur is widely accepted in steelworks laboratories,[1] its accuracy depends to a large extent on the calibration standards used.[2] The gravimetric method employing barium sulphate has been used for standardization despite its lack of sensitivity and accuracy. Samples containing less than 0.005% sulphur cannot be analysed by this method.[2]

Isotope dilution mass spectrometry (IDMS) has already been used for the precise determination of sulphur in heat-resisting alloys and alloy steels[3] but carbon steels, which can evolve hydrogen sulphide during dissolution, could not be analysed. To determine sulphur accurately, it must all be converted into sulphate in the dissolution of the sample.

In the present study sulphur is recovered as barium sulphate which is then converted into sulphur dioxide by thermal decomposition in a vacuum. Complete conversion of sulphur into sulphate during dissolution (which cannot be ascertained by the gravimetric method) is obtained. The method has been applied to a number of standard samples from British Chemical Standards (BCS), Japanese Standards of Iron and Steel (JSS), National Bureau of Standards (NBS) and Japan Atomic Energy Research Institute (JAERI).

The principle of the IDMS method has been described elsewhere.[4] The most attractive feature of this technique is the fact that chemical separation and recovery need not be quantitative after the spike has been mixed with the sample, because the result depends only on the measurement of the isotope ratio. This eliminates many sources of error existing in the gravimetric method, *e.g.*, co-precipitation, occlusion and solubility.

EXPERIMENTAL

Apparatus

Apparatus used for the thermal decomposition of barium sulphate is shown in Fig. 1. It is a modification of that reported by Holt *et al.*[5]

Isotopic analysis of sulphur was performed with a CEC 21-103C mass spectrometer equipped with a Cary 401 vibrating reed electrometer and a recorder. This gives replicate $^{34}S/^{32}S$ measurements with a relative standard deviation of better than 0.2%.

Reagents

Reagent grade chemicals were used except for hydrochloric and nitric acids which were of super special grade.

Spike solution. Five mg of elemental sulphur (45% enriched ^{34}S isotope, Oak Ridge National Laboratory) were burned in a 1-litre polyethylene bottle by the oxygen combustion method[6] and the products were absorbed in a mixture of 10 ml of 30% hydrogen peroxide and 20 ml of 0.2 *M* potassium hydroxide. When a solution of higher sulphur content was required the combustion and absorption were repeated with a further amount of the enriched sulphur (not exceeding 5 mg) the same bottle and solution being used. The resulting solution was boiled to decompose the residual hydrogen peroxide. After cooling, the solution was diluted to 100 ml with water, weighed and stored in weighing bottles. The concentration of sulphur was determined by the IDMS method, using a standard potassium sulphate solution prepared gravimetrically.

Barium chloride solution, 10%. The solution was filtered through a fine-texture paper before use, to keep the blank constant.

Procedure

Dissolution of sample and isolation of sulphur as barium sulphate. Dissolve 0.2–2 g of sample in 10–20 ml of 16*M* nitric acid and 1 ml of bromine in a 500-ml conical beaker, with addition of 10–20 ml of 6*M* hydrochloric acid in small portions, heating if necessary. After dissolution is complete, add a weighed aliquot of the spike solution. Boil the spike solution for several min and then evaporate to dryness on a

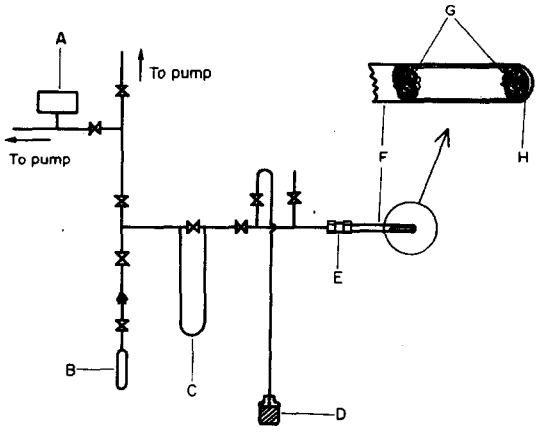

Fig. 1. Apparatus for thermal decomposition of barium sulphate. (A) vacuum gauge, (B) sampling bottle, (C) U-tube, (D) manometer, (E) Cajon union, (F) quartz tube, (G) quartz wool, (H) barium sulphate.

hot-plate at 250°. Evaporate with hydrochloric acid and bake to remove nitrate. Dissolve the residue in 10–20 ml of hydrochloric acid with heating. Dilute the solution to 50 ml with water, filter through medium-texture paper and precipitate the sulphate as barium sulphate by the addition of 10% barium chloride solution. Filter off the precipitate on a fine-texture paper and wash 3 or 4 times with water and ignite.

Decomposition of barium sulphate. Place the barium sulphate in an 8-mm bore quartz tube. Insert a plug of quartz wool to retain the barium sulphate. Slide the tube into a second, wider quartz tube sealed at one end and retain with a second plug of quarrtz wool as shown in Fig. 1. Attach the outer tube to a vacuum line by means of a vacuum-tight Cajon union (Cajon Co., Solon, Ohio). Flame the outer-tube under a vacuum of about 10^{-6} mmHg for at least 20 min to remove adsorbed materials. Then heat the end of the outer tube to the softening point of quartz for 10 min. Collect the evolved sulphur dioxide in a U-tube cooled with liquid nitrogen, pumping off other gaseous products. Transfer the sulphur dioxide to a sampling bottle by removing the liquid nitrogen from the trap, and keep for subsequent mass spectrometric analysis.

RESULTS AND DISCUSSION

The results of 5 independent spike calibrations are shown in Table 1. The standard deviation approaches the ultimate precision attainable by the IDMS method, *i.e.*, the error arises in the isotopic measurement. The average value agrees with the theoretical value, calculated from the weight of the enriched ^{34}S isotope, confirming the validity of the method for the determination of sulphur in sulphate.

In the determination of sulphur in steels and alloys, only the dissolution process must be quantitative and no quantitative chemical separations after spiking are necessary. Many problems associated with co-precipitation, occlusion and solubility, which can lead to serious analytical errors, do not affect the result because only isotope ratios are measured. Therefore the operational procedure can be simplified and shortened, *e.g.*, reduction of iron with zinc[2] or hydroxylamine hydrochloride[7] can be dispensed with and there is no need to wash the barium sulphate precipitate thoroughly.

Various dissolution methods were tried for the complete conversion of sulphur into sulphate, *e.g.*, with and without the addition of oxidizing reagents such as bromine, potassium nitrate[7] and potassium chlorate.[8] Table 2 shows the results obtained for carbon steel, JSS 242-5. The blanks, which amounted to 1.5–4 μg of sulphur, were subtracted from the observed sulphur values. The blank value approaches the practical detection limit of the procedure. The dissolution in the presence of bromine gives complete conversion of sulphur into sulphate. When bromine is added after completion of the dissolution a low result is obtained, indicating that sulphur compounds are evolved during the dissolution. Potassium nitrate and potassium chlorate are less effective in the oxidation of sulphur to sulphate. Similar analytical results were obtained for carbon steel, BCS 232/2. The use of bromine in the dissolution was also necessary for complete oxidation.

No significant difference between the dissolution with and without bromine was observed for nickel–chromium steel, mild steel, chromium–molybdenum steel, high-speed steel, 13% chromium stainless steel and heat-resisting alloys, indicating that no sulphur was lost during the dissolution. It must be pointed out that the addition of bromine in the dissolution is necessary when carbon steels have to be analysed by the usual gravimetric method.

The results obtained for BCS, JSS, NBS and JAERI standard samples are shown in Table 3. Good agreement with results reported previously[3] is obtained for heat-resisting alloys. Our results for BCS samples are in good agreement with the certified values except for 20% tungsten high-speed steel, BCS 241/2 which is difficult to analyse by the barium sulphate gravimetric method because of its high tungsten content.[7] Our results for JSS and NBS samples tend to be lower than the certified values. The ratios of our results (including the results of previous work[3]) to

Table 1. Calibration of the spike solution

Calibration No.		Sulphur concentration of spike, μg/g
1		153.9
2		153.8
3		154.2
4		154.3
5		154.3
	Average	$154.1 \pm 0.2_3$
	Theoretical value*	153.3

* Calculated from the weight of the enriched ^{34}S isotope before the oxygen combustion.

Table 2. Determination of sulphur in carbon steel JSS 242-5, (certified value 0.031%C)* with various methods of dissolution

Acids used in dissolution	Oxidizing reagents added	Sample taken, *g*	S found, *μg/g*
20 ml of HNO_3‡	None	1.8048	234.8
	None	1.7940	227.0
	None	1.8157	228.3
	0.1 g of KNO_3	1.8240	255.1
	0.5 g of KNO_3	1.5270	270.8
	0.2 g of $KClO_3$	1.8542	257.8†
18 ml of fuming HNO_3 and 8 ml of HCl	None	1.2546	277.9†
4 ml of bromine water and 20 ml of HCl	1 ml of Br_2	1.5873	258.6†
20 ml of HNO_3‡	Afer dissolution, 1 ml of Br_2	1.7943	241.5
20 ml of HNO_3 and 1 ml of HCl	1 ml of Br_2	1.8075	277.2
10 ml of HNO_3 and 5 ml of HCl	1 ml of Br_2	0.8215	280.6
15 ml of HNO_3 and 5 ml of HCl	1 ml of Br_2 and 0.1 g of KNO_3	1.0045	281.0
		1.5076	280.4
		2.0027	278.9
20 ml of HNO_3 and 18 ml of HCl		1.5314	280.0

* Combustion method.
† Blank not determined.
‡ Carbon steel can be dissolved in nitric acid by heating; hydrochloric acid was added after the dissolution was complete.

Table 3. Determination of sulphur in standard samples

Sample	Certified value, %S	Present method (IDMS), *ppm* S		
		Average	*s*	No. of detns
0.1% S carbon steel, BCS 232/2	0.126	1209	10	7
Mild steel, BCS 455	0.061	618	2	4
13% Cr rustless steel, BCS 211/1	0.032	312	2	3
20% W high-speed steel, BCS 241/2	0.025	215	2.5	3
Carbon steel, JSS 242-5	0.031	280	1	6
Alloy steel, JSS 152-4	0.022	188	2	4
Ni-Cr steel, NBS 32e	0.021	181	1	4
Cr-Mo steel, NBS 133a	0.329	2601	34	4
Inconel 600, JAERI R5	0.004*	20	1.6†	2
Incoloy 800, JAERI R7	0.006*	41.5	0.3	3

* Standard value by JSS. Eleven laboratories participated in the analysis, all using the combustion method. Ranges are 0.002–0.006 for JAERI R5 and 0.004–0.008 for JAERI R7.
† Range of two determinations.

the certified values are 0.96–1.0 for BCS samples, 0.86–0.90 for JSS samples and 0.79–0.86 for NBS samples.

Ikeno and Otsuki previously compared the yields of sulphur in the standard samples of various countries, using the combustion–titration method and found that the values certified by NBS and JSS were too high by an amount somewhat larger than that for the BCS samples, which also agrees with our findings and suggests that there is systematic bias in the methods of standardization of BCS, JSS and NBS.

The present method is not suitable for routine analysis, but could be used as a reliable referee method, but similar to that described by Cali and Reed.[10]

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EXTRACTIVE PHOTOMETRIC DETERMINATION OF VANADIUM(V) AS THIOCYANATO AND AZIDO MIXED-LIGAND COMPLEXES WITH *N*-HYDROXY-*N*-*p*-CHLOROPHENYL-*N'*-(2-METHYL-4-CHLOROPHENYL) BENZAMIDINE HYDROCHLORIDE

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Summary—Ternary systems involving thiocyanate or azide (X) and *N*-hydroxy-*N*-*p*-chlorophenyl-*N'*-(2-methyl-4-chlorophenyl)benzamidine hydrochloride (HOAm) are used for the extraction–photometric determination of vanadium(V) as a $VOX_2(OAm)HOAm$ complex. A strong synergistic effect is observed. Mn(II), Cr(III), Ti(IV), Zr(IV), Mo(VI) and W(VI) do not interfere. The method has been applied to standard steel samples.

N-Hydroxy-*N*,*N'*-diarylbenzamides, which act as monobasic and bidentate chelating agents, have been used for gravimetric and photometric determination of transition metals.[1–5] They also react with vanadium(V) in carboxylic acid, phenol or aldehyde medium to give a 1:1 adduct extractable into chloroform.[6] *N*-Hydroxy-*N*,*N'*-diarylbenzamidines react with vanadium(V) in thiocyanate and azide media to give deep green and greenish-blue complexes respectively (in chloroform). *N*-Benzoylphenylhydroxylamine(BPHA) and its analogues[7–10] are useful reagents for determination of vanadium(V) but according to Shendrikar[11] the BPHA method suffers from serious interference by Mn, Cr, Ti, Zr, Mo and W. The present method has the advantage over the BPHA method that these elements do not interfere. The reagent used is *N*-hydroxy-*N*-*p*-chlorophenyl-*N'*-(2-methyl-4-chlorophenyl)benzamidine hydrochloride (HCPMCPBH).

EXPERIMENTAL

Reagents

Standard vanadium(V) solution was prepared by dissolving ammonium metavanadate in doubly distilled water and standardized titrimetrically.[12]

HCPMCPBH was prepared by condensation of equimolar quantities of *N*-(2-methyl-4-chlorophenyl)-benzimidoyl chloride and *N*-*p*-chlorophenylhydroxylamine in ether medium.[1,13] The resulting hydrochloride was recrystallized from absolute ethanol: m.p. 188°; yield 80% (found: C 58.5%, N, 6.8%, H 4.1%; calculated for $C_{20}H_{17}N_2OCl_3$: C 58.53%, N 6.82%, H 4.14%). It was used as a 0.1% solution in chloroform.

Procedure

Take a solution containing up to 100 μg of vanadium(V) in a 100-ml separatory funnel, add 5 ml of 2% potassium thiocyanate or sodium azide solution and enough glacial acetic acid to make its concentration 2.0*M* in the final volume of 25 ml. Add 15 ml of 0.1% chloroform solution of the reagent and shake for 2 min. Transfer the organic phase to a 50-ml beaker. Wash the aqueous phase with two 4-ml portions of chloroform and add the washings to the contents of the beaker. Dry the combined extracts with 2 g of anhydrous sodium sulphate. Decant the extract into a 25-ml standard flask, washing the sodium sulphate with small portions of chloroform, and dilute to volume. Measure the absorbance at the wavelength of maximum absorption against chloroform as a blank.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the vanadium–HCPMCPBH complexes and of the reagent are shown in Fig. 1.

The vanadium–HCPMCPBH complex in the absence of thiocyanate or azide and at pH 3 in the absence of acetic acid shows a flat peak at 550–580 nm with a molar absorptivity of 1.3×10^3 $1.mole^{-1}.cm^{-1}$. In acetic acid medium (1.0–10.0*M*) a 1:1 blue-violet adduct is formed, with λ_{max} at 580 nm and molar absorptivity 3.6×10^3 $1.mole^{-1}.cm^{-1}$. However, in the presence of thiocyanate and azide a ternary complex is formed, having λ_{max} at 610 and 590 nm with molar absorptivities of 6.5×10^3 and 5.6×10^3 $1.mole^{-1}.cm^{-1}$ respectively.

Effect of variables

Various water-immiscible organic solvents were tried. Benzene, toluene, carbon tetrachloride and chloroform all extracted the ternary complexes. Chloroform proved to be the most satisfactory because it gives high distribution ratios for the reagent and the ternary complexes.

The acidity of the aqueous phase was adjusted with glacial acetic acid, the optimum ranges for the thio-

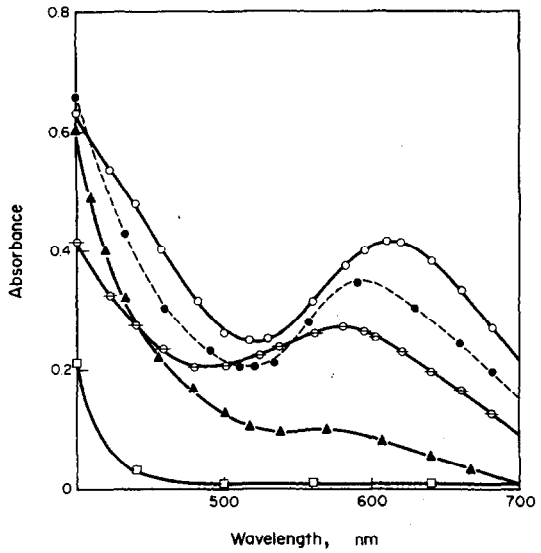

Fig. 1. Absorption spectra: —○——○ $6.28 \times 10^{-5}M$ V + reagent + thiocyanate; —●------● $6.28 \times 10^{-5}M$ V + reagent + azide; —◇——◇ $6.28 \times 10^{-5}M$ V + reagent + acetic acid; —▲——▲ $6.28 \times 10^{-5}M$ V + reagent; —□——□ $3.0 \times 10^{-3}M$ reagent.

cyanate and azide systems being 0–3.5 and 1.0–4.0*M* acetic acid respectively. A 5- and 10-fold molar ratio of *N*-hydroxyamidine to vanadium(V) was necessary for complete extraction of the thiocyanate and azide complexes respectively. The thiocyanate and azide need to be present in 10- and 120-fold molar ratio to vanadium respectively. Addition of up to a 5000-fold molar ratio of either did not affect the absorbance and λ_{max} of the ternary complex. The order of addition of reagents was not critical.

Sodium, potassium, ammonium and magnesium sulphates were tried as salting-out agents in the concentration range 1–3*M*, but did not enhance the extraction. The extracts were stable for at least 30 hr at 27 ± 2°. The period of shaking was varied from 1 to 5 min, and extraction was found to be quantitative in 1 and 2 min for the thiocyanate and azide systems respectively. It is therefore recommended to shake the mixture for at least 3 min.

Characteristics of the complexes

The thiocyanate and azide systems obeyed Beer's law up to 7.2 and 8.0 ppm of metal. The optimum concentration ranges on the basis of Ringbom plots[14,15] were 0.6–6.8 and 1.0–7.6 ppm of vanadium respectively.

The relative standard deviations (10 measurements, vanadium 4 ppm) were found to be 0.7 and 0.8% for thiocyanate and azide systems respectively.

The ratio of vanadium to *N*-hydroxyamidine was determined by the mole-ratio[17] and Job methods.[18] The ratio of thiocyanate to vanadium was determined by the mole-ratio[17] and slope-ratio methods[19] and that of azide by a curve-fitting method.[20] The results obtained show the formation of 1:2:2 (metal:reagent:thiocyanate or azide) ternary complexes.

Table 1. Tolerances* for foreign ions

Ion added	Thiocyanate system, *mg/ml*	Azide system, *mg/ml*
Fe^{3+}§	1.0	0.80
Cu^{2+}	0.15	0.1
Hg^{2+}	2.4	2.0
Pb^{2+}	1.5	1.7
Mn^{2+}	1.6	1.6
Zn^{2+}	2.4	2.0
Cd^{2+}	2.4	1.6
Pd^{2+}	0.5	0.5
Th^{4+}	2.0	1.6
Tl^{3+}	1.2	1.0
Al^{3+}	2.4	2.4
Cr^{3+}	1.5	1.5
Ni^{2+}	2.0	2.0
UO_2^{2+}	0.8	0.8
Co^{2+}	2.4	2.4
Ti^{4+}	0.2	0.18
Zr^{4+}	0.06	0.06
Mo(VI)	0.3	0.3
W(VI)	0.06	0.04
Nb(V)	0.1	0.12
Ta(V)	0.12	0.15
Bi^{3+}	0.8	1.0
Be^{2+}	1.2	1.2

* Amount causing < 2% error.
§ Masking with trisodium phosphate.

The complex must be neutral if it is extractable into chloroform, so the product is probably VOX_2-(OAm)(HOAm) where X is thiocyanate or azide, and OAm and HOAm are deprotonated HCPMCPBH and HCPMCPBH respectively.

Effect of other ions

The effect of foreign ions was studied with 4 ppm of vanadium in 2.0*M* acetic acid, by following the procedure above. The interference due to Fe^{3+} could be eliminated by masking with trisodium phosphate (5 g). Chloride, bromide, iodide, nitrate, sulphate, thiosulphate, triethanolamine, urea, thiourea, phthalate, borate, citrate, tartrate, alkali and alkaline earth metal ions, lanthanides, phosphate and arsenate did not interfere. The tolerance limits for other ions are shown in Table 1.

Table 2. Determination of vanadium in steels

Sample	Vanadium found, %*	Certified value, %	Std. devn., %
64a Alloy steel	1.55	1.57	0.009† 0.010§
241/1 High-speed steel	1.57	1.57	0.010† 0.0115§
252 Low-alloy steel	0.45	0.46	0.006† 0.006§

* Average of six determinations for each system.
† Thiocyanate system.
§ Azide system.

Determination of vanadium(V) in steel samples

To check the validity of the method, two tungsten–vanadium steels (64a and 241/1) and a tungsten-free low-alloy steel (252), obtained from Bureau of Analysed Samples, Ltd., Middlesbrough, England were analysed for vanadium(V). The results are shown in Table 2.

Steel samples containing up to 3 mg of vanadium were dissolved in 40% nitric acid. Since tungsten interferes if present in excess, it was removed as hydrated tungstic oxide, by filtration with Whatman No. 42 paper. The filtrate was made up to 250 ml with distilled water and vanadium(V) was determined by the procedure described.

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SPOT-TEST DETECTION OF ARYL HYDRAZINES, HYDRAZONES, OSAZONES, OXIMES AND AROMATIC AMINES

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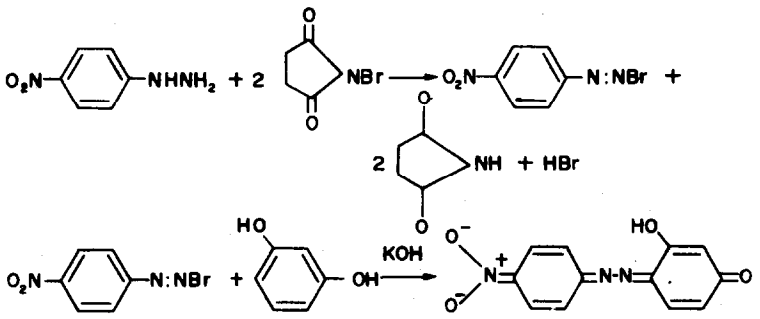
Summary—Arylhydrazines are detected by oxidation with *N*-bromosuccinimide and coupling with resorcinol to form azo-dyes which are intensely coloured in alkaline media. Hydrazones and osazones are hydrolysed to form the arylhydrazines, which are then tested for 4-Nitro- and 2,4-dinitrophenylhydrazines are tested for by forming their hydrazone with salicylaldehyde and adding alkali to produce a violet colour. The hydroxylamine formed by the hydrolysis of oximes is oxidized by iodine monochloride in the presence of sulphanilic acid; coupling with 8-hydroxyquinoline forms a dye that is red in alkali. Intense colours are immediately produced when primary, secondary and tertiary aromatic amines are mixed with diacetoxyiodobenzene. All the tests are sensitive and appear to be specific.

Feigl and Demant[1] detected arylhydrazines by oxidation with selenious acid and reaction with 1-naphthylamine to form a red or red-violet colour. With relatively large amounts of arylhydrazine, red selenium precipitates. On boiling with arsenic acid or an organic arsonic acid, arylhydrazines form phenol which can be coupled with 2,6-dichloroquinone-4-chloroimine; the condensation product turns blue on exposure to ammonia.[2] Phenylhydrazine has been noted to yield a yellow colour with pyridine-2-aldehyde,[3] but, it was not possible to observe the colour change with 4-nitro and 2,4-dinitrophenylhydrazines, since they are themselves orange.

A sensitive and specific test for arylhydrazines is described. On reaction with *N*-bromosuccinimide, arylhydrazines form the corresponding diazonium salts, the azo-dyes of which, formed by coupling with resorcinol, are deeply coloured in alkaline medium. With 4-nitrophenylhydrazine the reactions are:



Other compounds containing nitrogen do not interfere.

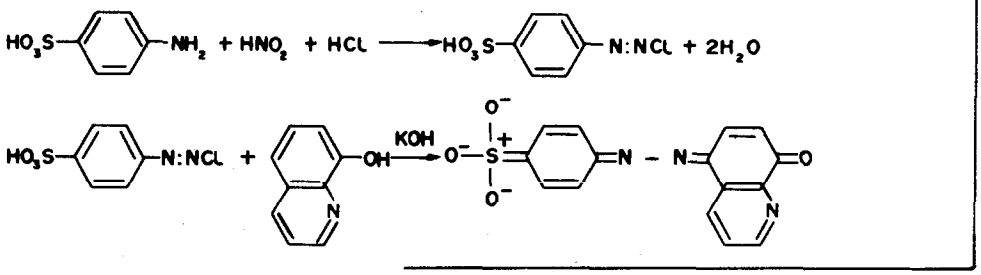
This test has been applied to the detection of arylhydrazones and oximes, involving hydrolysis with concentrated hydrochloric acid to split off the arylhydrazine hydrochloride, which is stable on boiling, then carrying out the test as described.

It has also been found that the 4-nitro and 2,4-dinitrophenylhydrazones of salicylaldehyde give a violet colour with potassium hydroxide, suitable for their detection.

Aldoximes and ketoximes split off hydroxylamine hydrochloride on warming with hydrochloric acid, and this can be detected by oxidation with iodine monochloride to nitrous acid in the presence of sulphanilic acid (which is then diazotized) and coupling

bright red in alkali. The following reactions occur:

$$NH_2OH + 2ICl + H_2O \rightarrow HNO_2 + 2HI + 2HCl$$



Any iodine that may appear by the reaction of hydriodic acid with surplus iodine monochloride need not be bleached as in alkaline medium it gives only a faint yellow colour and does not interfere with the test.

Most arylamines undergo coupling reactions with diazonium salts to form azo compounds,[4] and primary amines, after diazotization, couple with 2-naphthol to yield coloured products.[5] A dithiocarbamate test for secondary amines[6] and a very selective test for tertiary amines, employing citric acid–acetic anhydride,[7] have been reported. Colour reactions of aromatic amines with ceric sulphate[8] and lead tetra-acetate[9] have also been described.

A specific and sensitive test for detecting primary, secondary and tertiary aromatic amines is described. Intense colours are immediately produced when diacetoxyiodobenzene is mixed with an aromatic amine. This colour reaction is due to the formation of symmetrical azo-dyes, together with some other oxidation products, from primary amines. With secondary amines, the diarylnitrogen radical is probably formed. Tertiary amines appear to undergo oxidative dealkylation.[10]

No aliphatic or alicyclic amine or other nitrogen-containing compound tested gave coloured products.

EXPERIMENTAL

Reagent

Diacetoxyiodobenzene solution, ca. 1%. Prepared by dissolving the commercially available material in glacial acetic acid, or by mixing 5 ml of acetic anhydride with 1 ml of 20-vol hydrogen peroxide in a ground-glass stoppered flask, shaking well, and after 1 hr adding 1 ml of iodobenzene and letting stand for 30 min before dilution to 100 ml with glacial acetic acid. The solution is stable for 3 months.

Procedures

Detection of arylhydrazines. A drop of test solution in 0.1*N* hydrochloric acid is placed in a depression on a spot-plate and mixed successively with one drop each of 0.5% *N*-bromosuccinimide and 1% aqueous resorcinol solution. A red to red–violet colour appearing on the addition of 1 or 2 drops of 5% potassium hydroxide solution is a positive test.

Detection of arylhydrazones or osazones. A drop of test solution or a crystal of the solid is mixed with a few drops of concentrated hydrochloric acid in a micro-crucible and the mixture evaporated nearly to dryness. The residue is dissolved in a drop of water and the arylhydrazine is detected as above.

Detection of 4-nitro or 2,4-dinitrophenylhydrazine. A drop of test solution in methanol or 0.1*N* hydrochloric acid is placed on a spot-plate and treated with a drop of 1% solution of salicylaldehyde in methanol. Addition of 1 or 2 drops of 5% potassium hydroxide solution results in a violet colour if the test is positive.

Detection of oximes. A crystal of the solid is heated with 1 or 2 drops of concentrated hydrochloric acid in a micro-crucible till the liquid is just evaporated. Then 1–2 mg of sodium acetate, a drop of 1% sulphanilic acid solution and 1 or 2 drops of 1% solution of iodine monochloride in 0.1*M* hydrochloric acid are added. After 30 sec, a drop of 1% aqueous 8-hydroxyquinoline solution and 1 or 2 drops of 5% potassium hydroxide solution are added. An immediate development of a red colour indicates the presence of an oxime.

Detection of aromatic amines. A drop of test solution in methanol, acetonitrile, ethanol, dioxan, acetone or glacial acetic acid is placed on a spot-plate and treated with a drop of diacetoxyiodobenzene solution. Immediate formation of an intense colour is a positive test.

Sulphanilic acid is dissolved in water for the test.

RESULTS

The following compounds have been tested and give the colours and detection limits (in μg) shown in parentheses.

Arylhydrazines. Phenylhydrazine (red, 0.03) and its 2,4-dinitro (violet, 0.02), 2-nitro (red, 0.05), 3-nitro (red, 0.05), 4-nitro (violet, 0.02), 4-bromo (orange, 0.1), 2,4,6-tribromo (red, 0.1) and 4-chloro (red, 0.05), 4-sulphonic acid (red–violet, 0.05) and 2-carboxylic acid (red, 0.08) derivatives and 1-naphthylhydrazine (red, 0.03).

Arylhydrazones. Acetophenone-2,4-dinitrophenylhydrazone (violet, 0.03), acetone-4-nitrophenylhydrazone (violet, 0.03), salicylaldehyde-2,4-dinitrophenylhydrazone (violet, 0.02) and benzaldehydephenylhydrazone (red, 0.06).

4-Nitrophenylhydrazine (violet, 0.01) and 2,4-dini-

trophenylhydrazine (violet, 0.01) by salicylaldehyde test.

Osazones. Glucosazone (red, 0.1), maltosazone (red, 0.1), arabinose osazone (red, 0.08), galactose osazone (red, 0.1) and xylose osazone (red, 0.1).

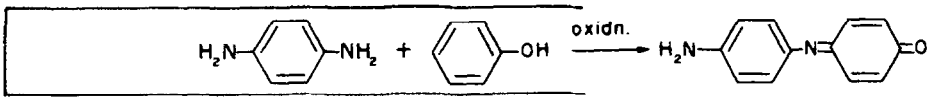
Oximes. Acetone oxime (red, 0.04), dimethylglyoxime (red, 0.01), salicylaldehyde oxime (red, 0.05) and benzil oxime (red, 0.02).

Aromatic amines. Aniline (purple changing to dark brown, 0.01), 2-, 3- and 4-toluidines (violet, 0.03), 2- and 4-anisidines (violet, 0.02), 2-chloroaniline (brown, 0.04), 3- and 4-chloroaniline (red-violet turning brown, 0.05), anthranilic acid (reddish-brown, 0.02), sulphanilic acid (deep red, 0.01), 2-aminobenzenethiol (dark brown, 0.04), 3-nitroaniline (red-brown, 0.08), sulphanilamide (deep red, 0.02), sulphadimidine (red-brown, 0.03), sulphathiazole (deep red, 0.01), sulphamerazine (red-brown, 0.04), sulphadiazine (red-brown, 0.03), sulphapyridine (red-brown, 0.03), diphenylamine (brown changing to green, 0.01), 2-phenylenediamine (brown changing to orange, 0.03), 3-phenylenediamine (deep red, 0.02), 4-phenylenediamine (green changing to dark brown, 0.01), 1- and 2-naphthylamine (deep red, 0.02), 4-aminosalicylic acid (red-brown, 0.05), 2,4,6-tribromoaniline (brown, 0.1), 4-aminobenzoic acid (violet, 0.02), *N*-phenylanthranilic acid (dirty green, 0.05), *N,N*-dimethylaniline (green, 0.04), 4-bromoaniline (red-brown, 0.04), *N,N*-diethylaniline (green, 0.03), 2-aminophenol (red-brown, 0.03), 3-aminophenol (red-brown, 0.04) and 4-aminophenol (violet, 0.02).

4-Dimethylaminobenzaldehyde (yellow, 0.1) gives a colour after 2 min. 2-Nitro and 4-nitroaniline, 2-aminopyridine and *N*-acetyl or *N*-benzoylaniline do not yield any colour.

Phenylhydroxylamine and *N,N'*-diphenylthiourea produce a faint yellow colour.

The test may be used to distinguish between the isomeric phenylenediamines. A further confirmation is provided if the test solution is mixed with a drop of 1% solution of phenol in glacial acetic acid prior to the addition of diacetoxyiodobenzene and developing the colour: 2-phenylenediamine (deep red, 0.02), 3-phenylenediamine (brown, 0.04) and 4-phenylenediamine (blue, 0.01). The colours are believed to be formed by the oxidative condensation of phenylenediamines with phenol at the *para* position, forming indophenol dyes, *e.g.*



The tests for arylhydrazines and aromatic amines can also be done on Whatman No. 1 paper.

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SOLID-STATE ION-SELECTIVE ELECTRODES FOR THE POTENTIOMETRIC DETERMINATION OF PHOSPHATE

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Summary—A number of solid-state ion-selective electrodes for the potentiometric determination of phosphate have been made and their properties investigated. The most successful of these electrodes, which had a membrane comprising silver sulphide, lead sulphide and lead hydrogen phosphate, had a theoretical Nernstian response to orthophosphate ion at concentrations down to 5 μg/ml total phosphate at pH 8.3. The electrode had a slow response and its standard potential changed with time. Anions such as sulphate, bicarbonate and nitrate did not interfere; chloride had a transient effect, but even at its worst the interference was less serious than with other phosphate electrodes. The electrode was used as an indicator in the potentiometric precipitation titration of phosphate and lanthanum.

Sodium phosphate is used to control the pH of boiler waters, so as phosphates tend to be deposited in high-pressure boilers, monitoring of the phosphate content of the boiler water is desirable. Phosphate-selective electrodes have been the subject of considerable investigation, but a number of liquid ion-exchange electrodes[1–3] and heterogeneous electrodes based on inorganic phosphate salts[4] were poorly selective. Silver phosphate electrodes[5] are too susceptible to interference by chloride for general use. A lead amalgam–lead hydrogen phosphate electrode[6] has been used in phosphoric acid solution, but having to keep the apparatus free of oxygen is a disadvantage of such a system. The present work concerns attempts to make solid-state phosphate-selective electrodes based on a lead-selective electrode.

THEORY

The phosphate-selective electrodes described here nave membranes composed of mixtures of sparingly soluble crystalline components with two different functions: (*a*) materials that make the membrane selective towards lead ions and (*b*) lead phosphate salts to provide an equilibrium concentration of lead ions when in contact with a solution of phosphate ions. The lead concentration is related to the phosphate concentration by means of the solubility product

$$K_s = [Pb^{2+}]^3\,[PO_4^{3-}]^2$$

and therefore the emf of the lead-selective electrode may be represented by either of equations (1) and (2), where k is a constant.

$$E = E^\circ + \frac{k}{2}\log[Pb^{2+}] \qquad (1)$$

$$E = E^\circ + \frac{k}{6}\log K_s - \frac{k}{3}\log[PO_4^{3-}]. \qquad (2)$$

In practice, a buffer is added to the sample solution so that, the pH being constant, the free phosphate concentration is a fixed proportion of the total phosphate concentration, C_p.

$$[PO_4^{3-}] = \phi \cdot C_p$$

where ϕ is a constant at a given pH and temperature. Substituting for $[PO_4^{3-}]$ in equation (2) gives

$$E = E^\circ + \frac{k}{6}\log K_s - \frac{k}{3}\log\phi - \frac{k}{3}\log C_p. \qquad (3)$$

The addition of the buffer also provides a medium of constant ionic strength, so it is valid to express equations (1)–(3) in concentration terms. The constant pH must neither be so high that lead hydroxide is precipitated nor so low that the lead concentration is controlled by the concentration of hydrogen phosphate ion through the solubility product $K'_s = [Pb^{2+}]\,[HPO_4^{2-}]$.

The lead-selective component of the membrane was either the PbS/Ag_2S mixture reported previously[7] or lead dioxide, for which the reaction is

$$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O.$$

The potential of a lead dioxide electrode is controlled by both the lead concentration and the pH, but as the latter is kept constant in the phosphate solution, lead dioxide should be a suitable material for the membrane.

EXPERIMENTAL

Apparatus

Potentials were measured with a high impedance millivoltmeter, either a Corning 110 digital pH-meter or a Keithley 604 electrometer with a Solartron LM 1420.2 digital voltmeter connected across its unity gain output terminals. The potentials were recorded on a Servoscribe chart-recorder.

A Radiometer F.3004 lead-selective electrode served as the basis for the phosphate-selective electrode; this electrode is of the "Selectrode" type.[7] A Radiometer K4025 saturated calomel electrode was used as reference electrode.

Reagents

Stock standard lead solution, 0.1*M*. Lead nitrate (16.56 g) dissolved in water and made up to 500 ml in a calibrated flask. Other lead solutions (10^{-2}–$10^{-5}M$) were prepared by successive dilution of the stock solution.

Stock standard phosphate solution, 0.1*M*. Anhydrous disodium hydrogen orthophosphate (7.078 g) or potassium dihydrogen orthophosphate (6.805 g) dissolved in water and made up to 500 ml in a calibrated flask. Other standard solutions (10^{-2}–$10^{-6}M$) were prepared by successive dilution of this solution.

Ammonia–ammonium acetate buffer. Ammonium acetate (38.54 g) dissolved in about 400 ml of water, adjusted to pH 8.8 by dropwise additions of concentrated ammonia solution and made up to 500 ml in a calibrated flask.

Preparation of membrane materials

Lead hydrogen phosphate. Lead nitrate (30 g) was dissolved in about 70 ml of water and the solution heated to boiling. Phosphoric acid (15 ml) was added to about 20 ml of water, mixed and made up to about 50 ml with water. This solution was slowly added to the boiling lead nitrate solution. The mixture was digested at 80–90° for 30 min and then allowed to cool. The white precipitate was filtered off, washed with cold demineralized water and dried at 50°.

Equimolar lead phosphate–lead sulphide mixture. Lead nitrate (30 g) was dissolved in about 100 ml of water. Anhydrous disodium hydrogen phosphate (5.7 g) and hydrated sodium sulphide (4.8 g) were dissolved in about 50 ml of water. This solution was filtered, the filtrate being allowed to drip into the lead nitrate solution. When all the phosphate/sulphide solution had been added, the supernatant liquor was decanted and the precipitate washed with four portions of demineralized water. The precipitate was then filtered off, again washed with water, and dried at 70°.

Lead sulphide–silver sulphide mixture. This equimolar mixture was supplied with the electrode.

Lead dioxide. Analytical reagent grade material (Hopkin and Williams Ltd.) was used.

Preparation of ion-selective membrane

Portions of the component materials were weighed out so as to give the desired molar ratios, mixed, and ground in an agate mortar. The mixture was rubbed into the surface of the electrode with a glass rod.

Potentiometric measurements

Phosphate solution (20 ml) and buffer solution (2 ml) were placed in a 50-ml beaker and stirred by a magnetic stirrer. The electrodes were immersed in the solution and the potential was recorded when a steady reading was obtained. Unless otherwise stated, the ammonium acetate buffer was used; this gave a pH of 8.4 when diluted as above. Measurements were made at room temperature.

RESULTS

Effect of membrane composition

Responses to both lead and phosphate ions were determined for electrodes with membranes of different compositions, before the performance of the best of these electrodes was investigated in greater detail.

Lead dioxide–lead hydrogen phosphate membranes. The membrane consisted of an equimolar mixture of the two components. The electrode had an approximately Nernstian response to lead ions (~27 mV per tenfold increase in concentration in the range 10^{-4}–$10^{-2}M$), but the response to phosphate ions was unstable and of low sensitivity. A freshly prepared electrode responded to changes in phosphate concentration, but its standard potential steadily decreased for some hours. By the time the electrode gave a stable emf at a given concentration, the sensitivity was only 7 mV per tenfold change in concentration between 10^{-3}–$10^{-4}M$ and was lost completely at concentrations below $10^{-4}M$.

Lead sulphide–silver sulphide–lead phosphate membranes. The membranes comprised two parts of the equimolar mixture of silver sulphide and lead sulphide and one part of the equimolar mixture of lead sulphide and lead phosphate, giving a final molar composition of 50% PbS, 33% Ag_2S and 17% $Pb_3(PO_4)_2$. The electrodes had sub-Nernstian responses to lead ions (about 24 mV per decade) and a very small and poorly reproducible response to phosphate ions.

Lead sulphide–silver sulphide membranes. The responses of electrodes with these membranes was almost Nernstian for lead ions (28 ± 1 mV per tenfold change in concentration) and approximately Nernstian for phosphate ions (15–20 mV per tenfold change in concentration). The response to phosphate ions, however, was too slow for useful measurements to be made routinely, *e.g.*, for a tenfold decrease in concentration the emf was still increasing after 2 hr.

On the basis of the solubility products of silver sulphide and lead sulphide, a phosphate response would not be expected, but electrodes with transition-metal sulphide membranes have limits of detection for metal ions much higher, at 10^{-8}–$10^{-7}M$, than would be predicted from the solubility products. One cause of this is oxidation of sulphides to soluble sulphates, with release of metal ions into solution.[8] Figure 1 shows that a $10^{-8}M$ concentration of lead ions would be sufficient to enter a solubility product equilibrium with phosphate under the conditions of these experiments and so make the electrode phosphate-sensitive.

Lead sulphide–silver sulphide–lead hydrogen phosphate membranes. Two different mixtures of the membrane components were prepared, having molar ratios of Ag_2S:PbS:$PbHPO_4$ of 1:1:1 and 1:1:2. The electrodes had an almost Nernstian response to lead ions in the concentration range 10^{-3}–$10^{-5}M$, the sensitivity being 28 ± 1 mV per tenfold change in concentration, while the sensitivity to phosphate ions was in the range 13–18 mV per tenfold change in concentration over the range 10^{-3}–$10^{-5}M$ total phosphate. The sensitivity indicated that the electrode was responding to the triply charged phosphate ion rather than the doubly charged hydrogen phosphate ion. The composition of the membrane did not affect the

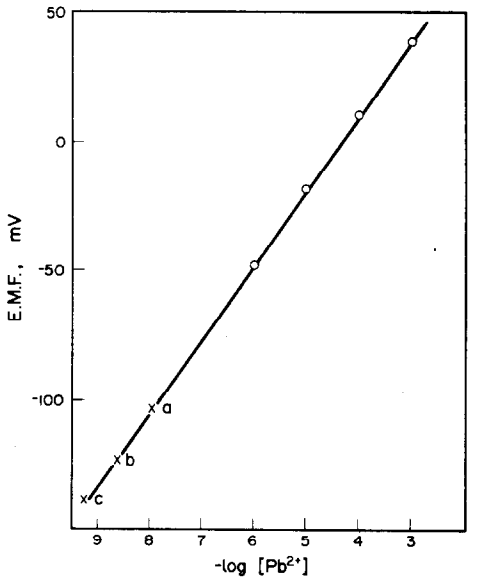

Fig. 1. Lead response of the phosphate-selective electrode. O Lead nitrate solutions, × calculated for (a) $10^{-5}M$, (b) $10^{-4}M$, (c) $10^{-3}M$ phosphate solutions.

sensitivity, but electrodes with the 1:1:2 mixture took about 30 min to reach equilibrium after a tenfold increase in concentration, which was about twice the time taken by electrodes with the equimolar mixture.

Performance of electrodes with equimolar lead sulphide–silver sulphide–lead hydrogen phosphate membranes

As electrodes with membranes of this composition were the best of those tested, their performance was investigated in greater detail.

Sensitivity. The responses of the electrode to lead and phosphate ions are shown in Figs. 1 and 2 respectively. The concentrations of lead in equilibrium with phosphate in the phosphate-containing solutions were calculated from literature data[9] and the observed pH of 8.36. Figure 1 shows that lead concentrations calculated in this way lie close to the extrapolated calibration line obtained with standard lead solutions, confirming the solubility product mechanism. Figure 2 shows the phosphate response of the electrode close to its limit of detection. The response was Nernstian down to $2 \times 10^{-5}M$ phosphate, but the sensitivity decreased at lower concentrations and was not reproducible.

Precision. The within-batch standard deviations of the response of the electrode to 10^{-3} and $10^{-4}M$ phosphate solutions were estimated from the differences between pairs of emf readings on 7 separate days to be ± 2 mV at $10^{-3}M$ and ± 4 mV at $10^{-4}M$ phosphate concentration, equivalent to relative standard deviations of approximately 30% and 65% respectively for the concentrations calculated from the readings. The poorer precision for the less concentrated solution can be attributed in part to the difficulty of identifying an equilibrium potential when the electrode was responding to a decrease in concentration. The slow response and the drift in the standard potential contributed to this effect.

Response time. Figure 3 shows, for both lead and phosphate solutions, the response curves resulting from the transfer of an electrode between 10^{-3} and $10^{-4}M$ solutions of the same ion. The lead response was much faster than the phosphate response, which tended to become slower as the electrode aged, until the electrode took over an hour to reach equilibrium after a tenfold change in concentration.

Stability of standard potential. All the electrodes, when immersed in a given solution, tended to give increasing emf readings with age; the rate of increase was constant for each electrode (for periods of at least two weeks). As the rate was independent of concentration, it may be interpreted as a shift in standard

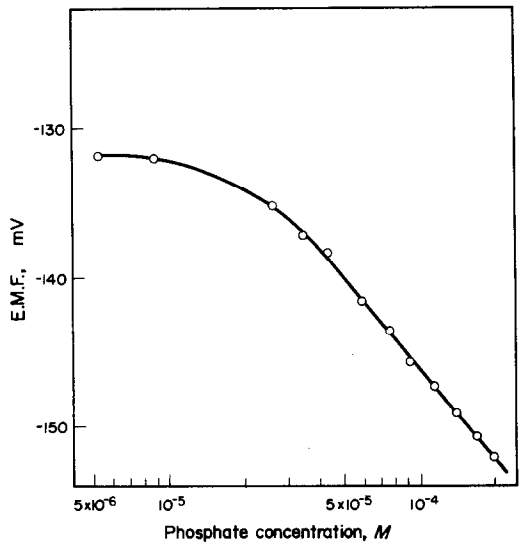

Fig. 2. Calibration of the phosphate-selective electrode.

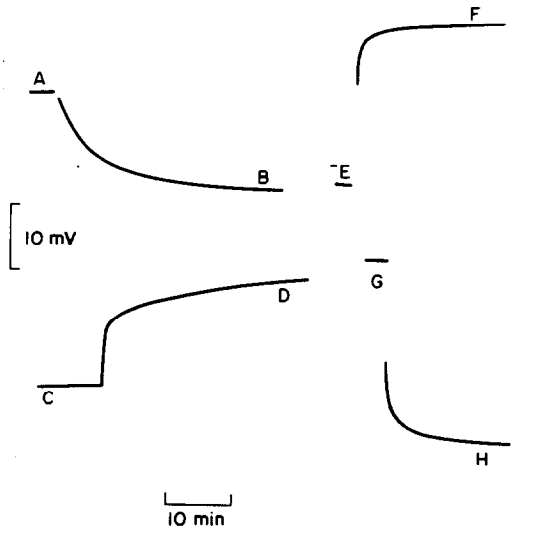

Fig. 3. Response curves for transfer of the phosphate-selective electrode between solutions. Phosphate solutions A–B 10^{-3}–$10^{-4}M$; C–D 10^{-4}–$10^{-3}M$. Lead solutions E–F 10^{-3}–$10^{-4}M$; G–H 10^{-4}–$10^{-3}M$.

Table 1. Effect of pH

	Readings, *mV*		
Total phosphate, *M*	pH 8.0	pH 8.4	pH 8.9
10^{-3}	−113.7	−121.9	−133.0
10^{-4}	−96.8	−105.3	−119.6

potential. The rate of drift was particular to each electrode and was not related to the treatment the electrode had received. The drift rates were in the range 1–6 mV/day. As the standard potential of the lead form (PbS/Ag_2S) of the Růžička "Selectrode" decreased at a rate of ~1 mV/day over a period of a month[10] and that of the Růžička Ag_2S/CuS copper "Selectrode" was stable,[8] it was assumed that the cause lay with the lead hydrogen phosphate in the membrane. Although the Nernstian slope factor corresponded to an orthophosphate response, a progressive transition from lead hydrogen phosphate to lead orthophosphate within the membrane was discounted as the cause of drift, because electrodes prepared with the orthophosphate showed similar shifts in standard potential.

Effect of pH. The effect of pH was tested by varying the proportions of ammonia and acetic acid in the buffer solution added to the phosphate solutions, so that the final pH values of solutions were 8.0, 8.4 or 8.9. The results in Table 1 show that the emf becomes more negative as the pH increases, corresponding to an increase in the proportion of orthophosphate ion in the solutions, *i.e.*, the log ϕ term in equation (3) increases.

Interferences. Interference effects were measured by injecting 100-μl portions of concentrated solutions of the interferents into 20 ml of $10^{-4}M$ phosphate plus 2 ml of ammonia-ammonium acetate buffer and observing the change in emf. This dilution would cause a shift of 0.035 mV, which was less than the discrimination of the pH-meter. Anions can interfere if they suppress the lead concentration below that arising from the dissolution of lead phosphate, *i.e.*, if

$$\left(\frac{K_{Pb_mX_n}}{[X]^n}\right)^{1/m} < \left(\frac{K_{Pb_3(PO_4)_2}}{[PO_4^{3-}]^2}\right)^{1/3} \qquad (4)$$

or if they form complexes with lead so that more phosphate dissolves from the electrode.

The results in Table 2 show that fluoride, sulphate and bicarbonate ions did not interfere under the conditions tested, as expected from relationship (4).

The chloride interference was characterized by a rapid change in emf on injection of the chloride solution, followed by a gradual return to the initial value. The interferences in Table 2 were calculated from the maximum deviation observed. Lead chloride is too soluble for the interference to arise on the basis of relationship (4) and chloro-complexes of lead are too weak to cause a significant dissolution of lead phosphate. A possible explanation is that the chloride ions form complexes with the lead ions in solution more rapidly than the lead ions can be replaced by dissolution of lead phosphate. The decrease in free lead concentration causes the emf to change as if the phosphate concentration had increased. As the lead phosphate slowly dissolves, the emf is restored to virtually its former value, since the effect of chloride ions at equilibrium is so small. Calculations with the stability constants for lead chloro-complexes[11] predict maximum apparent increases in phosphate concentration of 5, 40 and 100% at chloride concentrations of 7.5×10^{-4}, 6×10^{-3} and $1.5 \times 10^{-2}M$ respectively. These figures are in fair agreement with the experimental values in Table 2, except at the lowest concentration. Because of the non-equilibrium nature of the interference, initial local variations in chloride concentration at the membrane surface could produce different effects from those calculated by using the mean chloride concentration.

The negative nitrate interference can be explained with only 1% error by changes in activity coefficients caused by the increase in ionic strength on addition of the concentrated nitrate solution, i.e., the observed effect was caused by changes in solution equilibria

Table 2. Anionic interferences in $10^{-4}M$ phosphate solution

Anion	Concentration, *M*	Apparent phosphate concentration, *M*
F^-	5×10^{-4}	1×10^{-4}
NO_3^-	5×10^{-3}	9.4×10^{-5}
	1×10^{-2}	8.9×10^{-5}
SO_4^{2-}	5×10^{-4}	1×10^{-4}
Cl^-	7.5×10^{-4}	*1.24×10^{-4}
	6×10^{-3}	*1.57×10^{-4}
	1.5×10^{-2}	*1.64×10^{-4}
HCO_3^-	2.84×10^{-4}	1×10^{-4}

* Maximum value recorded (see text).

rather than being a property inherent in the electrode. Activity coefficients were calculated from a form of the Davies equation[12]

$$-\log f_{PO_4} = 9 \times 0.511\{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0.3I\},$$

where I is the ionic strength.

Effect of different buffer solutions. To check that the response of the electrode was not adversely affected by interactions of lead ions with either the acetate ions or the ammonia in the buffer, a number of other buffer solutions were tried.

Buffers such as triethanolamine + nitric acid (pH 7.5) and 3-(*N*-morpholino)propanesulphonic acid + sodium hydroxide (pH 8) gave similar results to the ammonia–ammonium acetate buffer. Citrate buffer (pH 6.7) gave very low sensitivities and in triethanolamine (pH 9.0) and borax (pH 9.2) buffers the sensitivity was almost completely lost and the electrode potential drifted persistently. The ammonia–ammonium acetate buffer was preferred for all the other work reported in this paper.

Use of the phosphate-selective electrode in potentiometric titrations

Phosphate can be determined, in principle, by potentiometric titration with silver or lead ions, a silver or lead-selective electrode, respectively, being used as the indicator electrode. The likelihood of interference by chloride with silver or sulphate with lead often makes these titrations unattractive in practice. A phosphate-selective indicator electrode should enable the titrant to be chosen independently of the nature of the electrode and having regard only to possible interaction of the titrant with other substances present in the sample.

Lanthanum has two advantages as the titrant. It interacts only weakly with most inorganic anions, with the principal exception of fluoride, so that interferences are less likely than in titrations with silver or lead. In addition, the titration curve for lanthanum phosphate precipitation should be symmetrical with a point of inflection coincident with the end-point, in contrast to titrations of phosphate with bivalent or univalent cations.[13]

Phosphate solutions were titrated with 10% lanthanum solution ($0.714M\ l^{-1}\ LaCl_3$). Curve A in Fig. 4 shows that in the presence of ammonia–ammonium acetate buffer the titration curve has a fairly sharp end-point break but is asymmetric. The cause of this asymmetry is probably associated with the performance of the electrode at low concentrations of phosphate, when the calibration curve deviates from linearity. In the absence of buffer, large end-point breaks are observed (curves B and C, Fig. 4), but at volumes that fall increasingly below the equivalence volume with decreasing pH in the sample solution. In unbuffered solutions, hydrogen ions are displaced from the hydrogen phosphate and dihydrogen phosphate as the lanthanum phosphate is precipitated. As the pH falls, the proportion of the dissolved

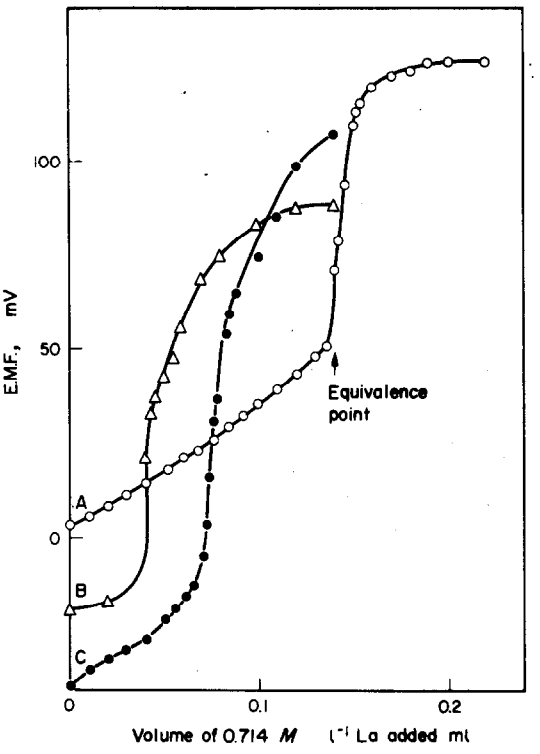

Fig. 4. Titration of (A) 10 ml of $10^{-2}M$ Na_2HPO_4 + 2 ml of buffer, (B) 5 ml of $10^{-2}M$ KH_2PO_4 + 5 ml of $10^{-2}M$ Na_2HPO_4 (C) 10 ml of $10^{-2}M$ Na_2HPO_4 with lanthanum chloride solution.

phosphate present as PO_4^{3-} will decrease and therefore each addition of lanthanum causes a reduction in PO_4^{3-} concentration by protonation as well as by precipitation. As a result, the emf changes more rapidly and a non-stoichiometric end-point break is obtained. Provided the sample solution is buffered, the electrode is useful as an indicator in potentiometric precipitation titrations for phosphate ions.

DISCUSSION

The best of the various phosphate electrodes tested was that based on a mixture of silver sulphide, lead sulphide and lead hydrogen phosphate, and this had several advantages over other types of phosphate-selective electrode. The electrode has a theoretical Nernstian response to orthophosphate ion at concentrations down to $5 \times 10^{-5}M$, which is a lower value than has been reported for liquid ion-exchange electrodes[1,2] or for silver phosphate electrodes.[5] Commonly occurring ions such as nitrate and sulphate do not interfere as they do with liquid ion-exchange electrodes[2] and even the chloride interference is less serious than is the case with either liquid ion-exchange electrodes or electrodes incorporating silver phosphate. The disadvantages of the electrode include its slow response to changes in phosphate concentration and the shift of its standard potential with time, both of which contribute to the poor precision of the electrode for analysis by direct potentiometry.

The electrode is useful as an indicator electrode in potentiometric titrations. Precipitation titrations of phosphate with lanthanum are feasible and are not affected by some of the interferences, such as those by sulphate or chloride, found with other titrants and their corresponding indicator electrodes. Although the titration curves are non-theoretical, being asymmetric, the end-point may be detected fairly accurately, provided the sample solution is buffered at pH 8.0–8.5.

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APPLICATIONS DE LA COLORIMETRIE DE PRECISION A LA MICROANALYSE ELEMENTAIRE

DOSAGES DU RHENIUM, DU RHODIUM, DU TELLURE ET DU ZIRCONIUM

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Résumé—Pour le dosage du rhénium, le prélèvement analytique de masse (m) inférieure ou égale à 1 mg est brûlé dans l'oxygène en fiole de Schöniger. Pour les dosages du rhodium ou du tellure ($m < 4$–5 mg) et du zirconium ($m < 1{,}5$ mg), le prévèlement analytique est attaqué par voie humide dans un micromatras du type Kjeldahl. Ces éléments sont dosés par spectrophotométrie en mettant en oeuvre les réactions suivantes: réduction de l'ion perrhenate par du chlorure stanneux en présence de furile-2,2′ dioxime ou de thiourée, formation d'un complexe rhodium(III)–hypochlorite de sodium, d'un iodotellurite, d'un complexe zirconium(IV)–orangé de xylénol.

La colorimétrie de précision, déjà mise en oeuvre dans notre Service pour de nombreux microdosages,[1–5] a été appliquée aux microdosages du rhénium, du rhodium, du tellure et du zirconium, dans les substances organiques, après combustion dans l'oxygène en fiole de Schöniger* (rhénium) ou attaque par voie humide (rhodium, tellure, zirconium).

Les complexes ou ions colorés auxquels il est fait appel pour les dosages colorimétriques sont indiqués ci-après.

Rhénium

Deux méthodes sont utilisées: la première, plus sensible, est préférable pour l'analyse des substances à faibles et moyennes teneurs en rhénium, la deuxième est plus appropriée à l'analyse des substances à fortes teneurs. Toutefois l'exactitude de la première méthode a été testée avec des substances à fortes teneurs faute de substances de références convenables.

Première méthode. La réduction du perrhénate par du chlorure stanneux en présence d'un grand excès de furile -2,2′ dioxime (souvent appelée α-furildioxime) donne lieu à la formation d'un complexe rhénium–dioxime rose, rose violacé ou rouge selon la teneur en rhénium.[7]

Deuxième méthode. La réduction du perrhénate par du chlorure stanneux en présence de thiourée donne lieu à la formation d'un complexe jaune.[8]

* Ce procédé a aussi été préconisé pour le tellure par Clark *et al.*[6] mais n'a pas été essayé dans notre Service.

Rhodium

L'hypochlorite de sodium forme un complexe bleu avec le rhodium(III).[9] Cette méthode a tout de suite donné satisfaction et, de ce fait, aucune autre n'a été essayée bien qu'il en existe de nombreuses (Beamish[10]).

Tellure

L'iodure de potassium forme un complexe grisâtre (iodotellurite TeI_6^{2-}) avec le tellure(IV).[11] Pour obtenir des résultats satisfaisants, nous avons dû ajouter du sulfite de sodium comme dans le cas du dosage colorimétrique du palladium[4,12] sous forme de PdI_4^{2-}. Plusieurs autres mèthodes ont ètè auparavant essayées et abondonnées par manque de précision à savoir:

—titrage du tellure(IV) par le thiosulfate de sodium selon la méthode de Johnson et Frederickson;[13]

—colorimétrie du bichromate de potassium non consommé dans l'oxydation du tellure(IV) en tellure(VI) par ce réactif selon Ma et Zoellner;[14]

—colorimétrie donnant lieu à la formation d'un complexe jaune par action de la thiourée sur le tellure(IV).[15]

Zirconium

L'orangé de xylénol[16] forme un complexe jaune orangé avec le zirconium(IV). La colorimétrie avec emploi de SPADNS,[17] trop sensible à l'influence de

l'acide sulfurique, n'a pas été adoptée. Le violet de pyrocatéchol, selon le procédé de Young[18] qui comporte l'introduction de gélatine et qui est plus précis que le procédé de Flaschka et Farah[19] donne des résultats acceptables, mais le mode opératoire est plus compliqué et les résultats moins précis qu'avec l'orangé de xylénol.

PARTIE EXPERIMENTALE

L'attaque par voie humide du type micro-Lorenz modifié, qui fournit la "solution d'attaque" après dilution du contenu du matras, les prélèvements, la préparation de "blancs de solution d'attaque"*, de "solutions d'essais à blanc de réactifs", les prélèvements d'aliquotes, la préparation de solutions étalons†, ont été antérieurement décrits dans une publication de Debal *et al.*[4]

La colorimétrie est effectuée sans recours à une courbe d'étalonnage. La quantité inconnue d'élément P mg contenue dans la fiole de colorimétrie est calculée à partir de p par une simple règle de proportionnalité:

$$P = \frac{pD}{d}$$

où D est l'absorbance de la solution inconnue et d la moyenne des absorbances de solutions étalons contenant p mg d'élément. Toutes les absorbances sont mesurées par rapport à des "solutions d'essais à blanc de réactifs".

Pour le dosage du rhénium, l'oxyde de rhénium Re_2O_7 étant volatil, l'attaque par voie humide en matras n'est pas applicable. La substance est brûlée, dans l'oxygène,[8,20] en fiole de Schöniger de 500 ml, du même type que celle utilisée par Lévy et Debal[2] pour le microdosage du fluor; cependant cette fiole est en verre borosilicaté (Pyrex), l'emploi de la silice plus onéreuse, étant superflu.

Réactifs

Les réactifs sans mention spéciale sont des réactifs Prolabo "pour analyses". Les réactifs employés tant pour l'attaque par voie humide ou par combustion que pour la colorimétrie sont cités sous la rubrique "Attaque". L'eau utilisée est distillée au laboratoire dans un appareil en acier inoxydable.

Rhénium

Attaque par combustion. Carré de papier d'environ 33 mm de côté muni d'une languette d'environ 35 mm de long en papier filtre noir "Whatman 29 qualitative". Le papier découpé peut être acheté sous le nom de "Sample Wrappers, black, no. 6514-F 65, A. H. Thomas Company, Philadelphia, PA 19105, U.S.A.). Glucose; chlorate de potassium.

Solution absorbante: 1 ml d'hydroxyde de sodium 0,25M et 5 ml d'eau lorsque l'attaque est associée à la colorimétrie avec emploi de furile-2,2' dioxime ou 10 ml d'hydroxyde de potassium 0,5M lorsque l'attaque est associée à la colorimétrie avec emploi de thiourée. Les solutions d'hydroxyde sont à préparer tous les 2 jours et ces mêmes solutions doivent être utilisées pour la colorimétrie.

Colorimétrie. Solution titrée de rhénium à 0,050 mg/ml:[21a,22] introduire 0,050 g de rhénium en poudre à 99,9% dans un matras de Kjeldahl identique à ceux utilisés pour les attaques du type micro-Lorenz. Ajouter 1,5 ml d'acide nitrique (p.s. = 1,38). Laisser le rhénium se dissoudre à froid pendant 30 mn environ puis ajouter 1 ml d'acide chlorhydrique (p.s. = 1,19) et un petit fragment de plaque de verre fritté porosité no. 1 pour régulariser l'ébullition. Porter à ébullition douce sur une rampe de minéralisation utilisée pour les attaques du type micro-Lorenz. Effectuer plusieurs additions d'acide chlorhydrique (0,5 à 1 ml) pour chasser les vapeurs nitreuses et éviter d'obtenir un extrait sec susceptible de provoquer des pertes de rhénium. Agiter souvent le matras pour faciliter l'élimination des vapeurs nitreuses. Lorsque celles-ci sont totalement chassées, laisser refroidir, transvaser dans une fiole jaugée et ajuster à 1 litre avec de l'eau. S'il y a plusieurs jours d'intervalle entre 2 séries d'analyses, conserver de préférence la solution titrée au réfrigérateur.

(1) *Méthode avec emploi de furile-2,2' dioxime*

Acide chlorhydrique, (p.s. = 1,19), et 6M acétone.

Chlorure stanneux: solution à 10% renouvelée par préparation tous les 8 jours. Peser 10 g de chlorure stanneux cristallisé $SnCl_2$, $2H_2O$ et ajouter 10 ml d'acide chlorhydrique (p.s. = 1,19). Compléter à 100 ml avec de l'eau. Faire chauffer éventuellement jusqu'à température voisine de l'ébullition si la solution est trouble, elle devient alors limpide. Arrêter aussitôt le chauffage et laisser refroidir.

Furile-2,2' dioxime: dissoudre 0,70 g de furile-2,2' dioxime dans 200 ml d'acétone. Préparer quotidiennement ce réactif.

(2) *Méthode avec emploi de thiourée*

Acide chlorhydrique (p.s. = 1,19); acide sulfurique 1M.

Chlorure stanneux: solution renouvelée par préparation tous les 8 jours. Peser 22 g de chlorure stanneux cristallisé $SnCl_2$, $2H_2O$ et ajouter 100 ml d'acide chlorhydrique 4M. Faire chauffer éventuellement jusqu'à température voisine de l'ébullition si la solution est trouble, elle devient alors limpide. Arrêter aussitôt le chauffage et laisser refroidir.

Phénolphthaléine: solution éthanolique à 0,1%.

Thiourée: solution aqueuse à 5%.

Rhodium

Attaque. Acide sulfurique (p.s. = 1,83); acide nitrique (p.s. = 1,38); eau oxygénée (110 vol).

Colorimétrie. Solution titrée de rhodium à 0,050 mg/ml: introduire 0,025 g de rhodium en poudre à 99,9% dans un bécher de silice garni de 1,2 g de pyrosulfate de potassium[21b] en poudre. Ajouter, par dessus, encore 1,2 g de pyrosulfate et faire fondre en chauffant doucement puis plus fort pendant 1 h environ. Laisser refroidir, ajouter encore 1,2 g‡ de pyrosulfate et chauffer doucement puis plus fort pendant 1 h environ et recommencer encore deux fois; s'il reste beaucoup de grains noirs non dissous continuer à chauffer. Laisser dans le bécher une tige de silice pour agiter de temps en temps pendant le chauffage le mélange fondu. Ajouter avec précautions sans laisser totalement refroidir 4 ml d'acide sulfurique (p.s. = 1,83) et chauffer très doucement 15 mn environ, jusqu'à dissolution. Ajouter encore avec précautions sans laisser totalement refroidir 3 ml d'acide sulfurique et chauffer 30 mn environ. Transvaser le lendemain le contenu du bécher et les eaux de rinçage de celui-ci dans une fiole jaugée de 500 ml et ajuster avec de l'eau. La solution est stable pendant plusieurs mois.

Hypochlorite de sodium: solution aqueuse à 5% préparée à partir de 250 ml "d'eau de javel" (Javel La Croix) à 48° chlorométrique et de 500 ml d'eau. Ce réactif dilué peut être conservé 8 jours dans un flacon brun et dans l'obscurité.

Solution tampon à pH = 5 environ: solution contenant 200 g d'acétate de sodium $NaCH_3COO$, $3H_2O$ et 50 ml d'acide acétique (p.s. = 1,05) par litre de solution aqueuse.

* Blanc de solution d'attaque: même mode opératoire que pour une attaque proprement dite mais sans introduction de substance à analyser.

† Solutions étalons: introduction dans les fioles de colorimétrie de p mg d'élément sous forme de solution titrée au lieu de solution d'attaque.

‡ Nous avons contrôlé que des quantités importantes de pyrosulfate de potassium ne gênaient pas la colorimétrie ultérieure.

Tableau 1. Attaques par voie humide

E*	m*	Opérations successives effectuées en micromatras
Rh	2 à 5	0,8 ml H_2SO_4 + 7 à 8 gouttes HNO_3; Eb* = 15 2 fois 7 à 8 gouttes HNO_3; Eb = 15 + 15 3 fois 8 à 9 gouttes H_2O_2; Eb = 15 + 15 + 15
Te	1 à 4	0,8 ml H_2SO_4 + 5 à 6 gouttes HNO_3: Eb = 15 2 fois 3 à 4 gouttes HNO_3; Eb = 15 + 15 3 fois 3 à 4 gouttes H_2O_2; Eb = 15 + 15 + 15
Zr	1 à 1,5	0,8 ml H_2SO_4 + 3 à 4 gouttes HNO_3; Eb = 15 2 fois 3 à 4 gouttes HNO_3; Eb = 15 + 15 3 fois 3 à 4 gouttes H_2O_2; Eb = 15 + 15 + 15

* Signification des symboles:

E: élément dosé dans des substances organiques.

m: masse du prélèvement analytique en mg. Si les teneurs en éléments sont faibles, il est possible d'élever m au-delà des valeurs indiquées.

Eb: durées d'ébullition exprimées en minutes. Ces valeurs sont données à titre indicatif; les vapeurs nitreuses doivent être totalement chassées lors de la dernière addition d'eau oxygénée. Eviter toute évaporation à sec.

Tellure

Attaque. Mêmes réactifs que ceux utilisés pour le rhodium. Masson[23] effectue seulement une attaque sulfonitrique mais cet auteur dose ensuite l'ion tellurite par argentométrie; dans une publication ultérieure[24] elle passe d'ailleurs en revue plusieurs méthodes de dosage du tellure.

Colorimétrie. Solution titrée de tellure à 0,050 mg/ml: pulvériser du tellure à 99,999% et en introduire 0,050 g dans un matras de Kjeldahl identique à ceux utilisés pour les attaques du type micro-Lorenz et ajouter 1,5 ml d'acide nitrique (p.s. = 1,38), maintenir au bain marie pendant 15 mn. Ajouter 5 ml d'acide nitrique et maintenir au bain marie pendant 1 h 30 mn. Prolonger éventuellement le chauffage de quelques dizaines de minutes supplémentaires s'il reste encore des vapeurs nitreuses ou quelques particules non dissoutes. Laisser refroidir, transvaser dans une fiole jaugée et ajuster à 1 litre avec de l'eau.

Iodure de potassium: solution 2M préparée quotidiennement.

Sulfite de sodium anhydre Merck *p.a.*: solution aqueuse à 0,8% renouvelée par préparation tous les 2 jours.

Acide chlorhydrique 2M.

Zirconium

Attaque. Mêmes réactifs que ceux utilisés pour le rhodium.

Colorimétrie. Solution titrée de zirconium à 0,200 mg/ml: dissoudre 0,3533 g d'oxychlorure de zirconium $ZrOCl_2$, $8H_2O$[21c] Merck pour analyses dans environ 300 ml d'eau. Ajouter immédiatement par petites portions 125 ml d'acide chlorhydrique (p.s. = 1,19). Ajuster à 500 ml avec de l'eau. La solution est stable pendant plusieurs mois.

Solution titrée de zirconium à 0,050 mg/ml: diluer avec de l'eau une partie de la solution précédente. Cette solution est stable pendant 3 semaines environ.

Acide chlorhydrique 1M; acide sulfurique 1,25M.

Orangé de xylénol, sel tetrasodique: solution aqueuse à 0,05%. La solution est stable pendant 4 jours environ.

Attaque par combustion, dosage du rhénium

Envelopper le prélèvement analytique de 0,5 à 1 mg, 2 à 3 mg de glucose et 3 mg de chlorate de potassium de façon classique dans le papier et introduire le tout dans le support de platine[2] solidaire du bouchon de la fiole de Schöniger. Effectuer la combustion comme pour le microdosage du fluor[2] en utilisant les solutions absorbantes indiquées à la section "*Reactifs*". Ouvrir la fiole de Schöniger 20 à 30 mn aprés la combusion aprés l'avoir agité. Transvaser immediatement la solution absorbante et les eaux de lavage (lavage à l'eau froide) de la fiole et du support soit directement dans la fiole de colorimétrie soit intermédiairement dans une fiole F si l'on doit procéder à des prélèvements de parties aliquotes.

Dans le cas du dosage avec emploi de thiourée, la solution absorbante est beaucoup plus basique que lors de l'emploi de la furile-2,2′ dioxime. Il convient donc de neutraliser sans attendre afin d'éviter de laisser la solution basique trop longtemps en contact avec le verre. Les produits de combustion du papier et des additifs (glucose et chlorate de potassium) ne perturbent pas le colorimétrie, il est donc inutile d'effectuer systématiquement un "blanc de combustion' (combustion sans introduction de substance à analyser) analogue au blanc de solution d'attaque. Il suffit que les fioles contiennent toutes les mêmes quantités d'hydroxyde d'où l'introduction de solution absorbante dans certaines fioles de colorimétrie (voir paragraphe suivant).

Attaque par voie humide dosage du rhodium, de tellure et du zirconium

Les méthodes différent légèrement selon les éléments à doser, elles sont reportées dans le tableau 1.

Colorimétrie

Les conditions de la colorimétrie sont reportées dans le tableau 2. Introduire les réactifs dans la fiole jaugée "de colorimétrie" de capacité f dans l'ordre indiqué dans la colonne R de ce tableau. Trois sortes de solutions sont ainsi préparées de façon similaire:[4] solutions inconnues, solutions étalons, solutions d'essais à blanc de réactif. Toutefois, introduire dans la fiole de colorimétrie,

—*dans le cas des solutions inconnues*

(1) soit le volume total $A = s$ ml de la solution d'attaque, soit lors des prélèvements de parties aliquotes des volumes $A = a_1 \ldots, A = a_i \ldots, A = a_n$ avec $a_1 > \ldots a_i \ldots > a_n$;

(2) un volume w de "blanc de solution d'attaque" avec $w = s - s = 0$, $w = a_1 - a_1 = 0$, $w = a_1 - a_i, \ldots, w = a_1 - a_n$ selon que $A = s$, $A = a_1, \ldots, A = a_n$.

—*dans les solutions étalons*

$A = v$ ml de solution titrée

$w = a_1$ ou s ml de blanc "de solution d'attaque" selon que l'on procède ou non au prélèvement de parties aliquotes.

—*dans les solutions d'essai à blanc*

$w = a_1$ ou s ml de "blanc de solution d'attaque".

Dans le cas du dosage du rhénium, les w ml de solution d'attaque sont remplacés par w ml de solution absorbante.

Lorsque le "blanc de solution d'attaque" est sans influence $w = 0$ dans tous les cas et n'est pas mentionné dans le tableau 2.

Calculs

Teneur centésimale en élément:

$$x = \frac{100\,PF}{ma_i}\%$$

RESULTATS ET DISCUSSION

Quelques résultats représentatifs des méthodes sont reportés dans le tableau 3. Il convient de noter la difficulté d'approvisionnement en substances de référence pures et stables pour le dosage du rhénium et du tellure.

Rhénium

Pour le dosage de cet élément Shanina *et al.*[8] emploient indifféremment, pour la combustion un

Tableau 2. Colorimétrie

E	*F**, *ml*	*f*, *ml*	*P*, *mg*	*DO**	*e*,* *cm*	*λ**, *nm*	*t**	*R*
Re	50	50	0,01 à 0,1 0,01 à 0,15	0,08 à 0,8 0,4 à 0,6	2 1	532	45 mn	*w* ml *A* ml HCl 6*M*: 4,7 ml furile-2,2′ dioxime: 13 ml chlorure stanneux: 5 ml H_2O
Re		100	0,1 à 0,5 0,5 à 1	0,1 à 0,5 0,25 à 0,5	2 1	390	50 mn	*w* ml *A* ml phénolphtaléine: 1 goutte H_2SO_4 1*M* jusqu'à virage (rose → blanc) HCl (p.s. = 1,19): 25 ml thiourée: 12 ml chlorure stanneux: 6 ml H_2O
Rh	50	50	0,02 à 0,5	0,03 à 0,8	2	665	3 h à 3 h 30	*w* ml *A* ml tampon: 5 ml hypochlorite de sodium: 25 ml H_2O
Te	50	50	0,02 à 0,5	0,03 à 0,7	2	550	20 à 30 mn	*A* ml H_2SO_4 (p.s. = 1,83): *x* ml† *V** = 30 ml HCl 2*M*: 5 ml sulfite de sodium: 2 ml iodure de potassium: 10 ml H_2O
Zr	50	50	0,005 à 0,025 0,025 à 0,05	0,1 à 0,4 0,2 à 0,4	2 1	535	1 h	*w* ml *A* ml HCl 1*M*: *X* ml† H_2SO_4 1,25*M*: (4-*x* ml)† orangé de xylénol: 4 ml H_2O

* Signification des symboles.
F: capacité de la fiole dans laquelle est dilué le contenu du matras dans le cas de prélèvements aliquotes.
DO: absorbance.
e: épaisseur de la cuve de colorimétrie.
λ: longueur d'onde à laquelle est effectuée la mesure.
t: temps d'attente avant la lecture de l'absorbance sur le spectrophotomètre.
V: volume approximatif de solution après addition d'eau.
F, *f*, *P*, *e*, *λ*, peuvent être éventuellement modifiés pour des cas particuliers.
† Voir "Resultats et discussion."

support de platine ou de silice. Le support de platine[2] (panier) utilisé pour le microdosage du fluor est satisfaisant lorsque son emploi est associé à l'addition de chlorate de potassium[20] et de glucose[2] tandis que le support de silice (spirale) est trop fragile pour une utilisation courante et provoque des combustions incomplètes (dépôts de charbon). Shanina *et al.*[8] font appel à une colorimétrie en présence de thiourée, après combustion en fiole de Schöniger garnie de 10 ml d'hydroxyde de potassium 0,5*M* comme solution absorbante. Afin d'appliquer sans modifications ce dosage colorimétrique, cette solution absorbante a été utilisée en association avec la colorimêtrie en présence de thiourée. L'hydroxyde de sodium beaucoup plus dilué, employé en association avec la colorimétrie en présence de furile-2,2′ dioxime, serait probablement utilisable mais n'a pas été essayé. Les substances organiques contenant du rhénium ayant tendance à laisser des résidus de combustion noirs, le papier Whatman indiqué serible préférable à un papier filtre sans cendres quelconque et de faibles masses de prélèvements analytiques (0,5 à 1 mg) sont souhaitables.

La précision des résultats est améliorée en ajoutant le chlorure stanneux et en ajustant le volume avec de l'eau immédiatement après l'addition de furile-2,2′ dioxime.

Plusieurs litres de solutions titrées de rhénium ont déjà été préparés sans rencontrer de difficultés selon le mode opératoire décrit alors qu'on aurait pu craindre à priori de perdre du rhénium par volatilisation de Re_2O_7. Ce mode opératoire est fondé sur ceux décrits dans les ouvrages de Duval[21a] et Busev.[22]

Rhodium

Le trichlorure de rhodium $RhCl_3$, $4H_2O$ permet la préparation rapide d'une solution de rhodium par simple dissolution dans l'eau puis addition d'acide sulfurique, mais le réactif étant hygroscopique, il con-

Tableau 3. Exemples de résultats

E	Composé	*m mg*	Teneur en élément, %* x_i	$\bar{x}$	*T*
Re	Rhénium carbonyle	1,047	57,5†		
		0,518	57,6†	56,8	57,07
		0,520	56,0†		—
		0,541	56,3†		—
		0,988	56,7†		—
		1,076	56,4§	56,8	
		1,011	56,7§		—
		1,038	57,7§		—
		1,018	56,5§		—
		1,001	56,4§		—
		0,634	57,2§		—
Rh	Triacétylacétonate de rhodium(II)	3,866	25,7	25,7	25,71
		3,500	25,5		—
		4,310	25,3		—
		2,755	25,7		—
		2,796	26,2		—
		3,148	25,7		—
Te	Composé de recherche (C, H, Cl, O, Te)	1,857	35,3	35,2	35,24
		2,075	35,9		—
		1,684	35,8		—
		2,061	34,7		—
		2,176	34,8		—
		1,838	34,7		—
Zr	Dicyclopentadienyledichlorure de zifconium	1,366	30,5	31,1	31,20
		1,074	30,9		—
		1,184	31,2		—
		1,035	31,1		—
		1,180	31,4		—
		1,123	31,3		—

* x_i: résultats trouvés.
$\bar{x}$: moyenne des résultats trouvés.
T: teneur calculée.
† Emploi de furile-2,2′ dioxime.
§ Emploi de thiourée.

duit à l'obtention de solutions à teneur en rhodium trop faible.

Comme il est difficile de se procurer des sels de rhodium purs et stables, la solution titrée doit être préparée à partir de rhodium. Il est cependant difficile de faire passer la totalité du rhodium en solution (grains noirs résiduels) d'où la nécessité de plusieurs opérations successives dont le nombre peut varier d'une préparation à l'autre en fonction de la quantité des grains noirs résiduels. La concentration de l'acide sulfurique utilisé pour le dissolution de la masse rhodium–pyrosulfate de potassium semble importante. En reprenant le masse rhodium–pyrosulfate de potassium par de l'acide sulfurique 9*M* au lieu d'acide sulfurique 18*M* (p.s. = 1,83), la teneur en rhodium de la solution ainsi obtenue était beaucoup trop faible.

Ayres[9] signale l'importance d'une addition rapide des réactifs pour le dosage colorimétrique. Nous avons confirmé cette remarque: il est indispensable d'ajouter l'hypochlorite immédiatement après l'introduction de la solution tampon et d'ajuster avec de l'eau.

Il convient d'autre part de prélever des parties aliquotes inférieures au tiers de la solution d'attaque. Des prélèvements trop importants de cette solution apportent des réactifs en quantités gênantes pour la colorimétrie.

Tellure

Pour le dosage colorimétrique de cet élément il est inutile de préparer un "blanc de solution d'attaque" mais les fioles de colorimétrie doivent toutes contenir la même quantité d'acide sulfurique soit 0,8 ml d'acide sulfurique (p.s. = 1,83).

Il faut donc introduire dans chaque fiole x ml d'acide sulfurique (p.s. = 1,83). Pour les solutions inconnues préparées à partir de la totalité de la solution d'attaque contenant déjà 0,8 ml d'acide sulfurique $x = 0$; pour celles préparées à partir d'un prélèvement aliquote de A ml contenant déjà $0{,}8A/50$ ml d'acide, $x = 0{,}8 - 0{,}8A/50$. Pour les "solutions d'essais à blanc" ne contenant pas d'acide sulfurique $x = 0{,}8$ ml. Dans les conditions opératoires définies sur le tableau 2 le loi de Lambert–Beer semble suivie au mieux à la longueur d'onde choisie de 550 nm.

Zirconium

Pour le dosage colorimétrique de cet élément, la présence d'acide chlorhydrique augmente légèrement l'absorbance. Comme les solutions titrées contiennent

une quantité d'acide chlorhydrique non négligeable, il convient d'ajouter dans les fioles ne contenant pas de solution titrée, X ml d'acide chlorhydrique $1M$ correspondant à l'acide apporté par le solution titrée. En général on introduit 1 ml de solution titrée de zirconium à 0,050 g/ml d'où $X = 0,7$ ml.

D'autre part, la quantité totale d'acide sulfurique $1,25M$ contenue dans chaque fiole devant être de 4 ml, il faut tenir compte des x ml d'acide sulfurique $1,25M$ déjà apportés par la solution d'attaque* soit:

$$x = \frac{11,5A}{50} \text{ avec } x \leqslant 4 \text{ ce qui entraîne } A \leqslant \frac{50 \times 4}{11,5}$$

Eléments gênants

L'influence de la présence simultanée d'éléments (quelques dixiémes de mg pour 1 ou 2 mg de prélèvement analytique) a été étudiée.

Dosage du rhénium. La présence de métaux qui souillent le support est défavorable. Il est souhaitable d'étudier au fur et à mesure chaque cas particulier qui se présente.

Dosage du rhodium. As, B, Br, Cl, Cr (solution d'attaque colorée en vert), Cu, F, Fe, Ge, Hg, K, N, Na, P, Pd (solution d'attaque colorée en jaune), S, Sn, ne gênent pas. Ag, Co, Pb gênent.

Dosage du tellure. Cl ne gêne pas. Des concentrations en phosphore et en fluor inférieures à 3 μg/ml ne gênent pas. Se gêne.

Dosage du zirconium. Al, Br, Ca, Cl, Co, Cr, Cu, I, Mn, N, Na, P, Pt, Sb ne gênent pas. Comme l'indique Cheng,[16] le molybdène ne gêne plus après addition d'acide ascorbique (10 mg par fiole de colorimétrie). Pd, Sn gênent.

CONCLUSION

Les méthodes de colorimétrie spectrophotométrique sont donc applicables au microdosage du rhénium, du rhodium, du tellure et du zirconium dans les substances organiques après attaque, mais dans l'ensemble les résultats obtenus sont moins précis que pour le microdosage d'éléments plus courants précédemment étudiés.[4,5]

* Un volume de 0,8 ml d'acide sulfurique (p.s. = 1,83 donc $18M$) utilisé pour l'attaque, ce qui correspond à 11,5 ml d'acide $1,25M$.

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Summary—The sample (< 1 mg) is burnt in an oxygen flask for the determination of rhenium. It is destroyed by a wet process in a Kjeldahl flask for the determination of rhodium or tellurium (sample < 4–5 mg) or zirconium (sample < 1.5 mg). These elements are determined spectrophotometrically. The following reactions are used: reduction of perrhenate by tin(II) chloride in the presence of 2,2'-furildioxime or thiourea, complexation of rhodium(III) by sodium hypochlorite, formation of iodotellurite, complexation of zirconium(IV) with Xylenol Orange.

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ION-EXCHANGER COLORIMETRY—IV MICRODETERMINATION OF BISMUTH IN WATER

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Summary—Ion-exchanger colorimetry for the microdetermination of bismuth(III) in water samples is described. The yellow bismuth–iodide complexes are specifically sorbed and concentrated on an anion-exchange resin in the sulphate form. The resin-phase absorbances at 492 and 700 nm are measured directly. Bismuth in the ppb–ppm range can be determined without interference, except in presence of a large amount of copper(II), silver(I) and lead(II). The detection limit is 6.4×10^{-9} *M*, *i.e.*, 1.3 ppb. The distribution ratio is larger than 10^7. It is, therefore, possible to enhance the sensitivity by increasing the sample volume. The method is useful for the determination of bismuth in natural waters and industrial effluents.

A new colorimetric method, "ion-exchanger colorimetry", which is sensitive, rapid and simple, has been reported by Yoshimura *et al.*[1–3] In this method an ion-exchange resin is employed both to concentrate the sample and to develop a coloured species. The absorbance of the coloured resin beads is then measured directly. The present paper is based on this method.

Several papers have described the colorimetric determination of bismuth.[4–7] The most widely used method is based on reaction of bismuth with iodide and extraction of the product from aqueous solution into 3-methylbutanol.[7] Other methods depend on preliminary concentration *e.g.*, solvent extraction, or masking or other procedures in order to compensate for the lack of sensitivity or selectivity. In contrast, the ion-exchanger colorimetry using the bismuth–iodide complex system described herein gives sufficient sensitivity and selectivity without such procedures. Moreover, this method offers simplicity and quickness in operation.

EXPERIMENTAL

Reagents

Standard bismuth(III) solution. Dissolve an appropriate amount of bismuth(III) sulphate in nitric acid and dilute to the required volume with demineralized water. Standardize the solution by EDTA titration.

Anion-exchange resin. Dowex 1-X2 (100–200 mesh and 200–400 mesh, sulphate form) was used. It was air-dried and stocked in polyethylene containers.

All other chemicals used were of analytical grade.

Apparatus

Hitachi recording spectrophotometer, Model EPS-3T, a perforated metal plate of absorbance 1.0 or 2.0 being used in the reference beam to balance the light intensities. All experiments were performed at room temperature.

Procedure for determination of bismuth

To a 200-ml water sample containing 0.22–1.6 μmole of bismuth, add 5 ml of concentrated sulphuric acid, 0.5 g of potassium iodide (Note 1), 1 ml of 0.1*M* sodium thiosulphate (Note 2) and 0.50 g of Dowex 1-X2 (100–200 mesh) in the sulphate form. Stir the solution for 10 min, collect the resin beads by filtration under suction and pack them into a 1-mm quartz cell (see Fig. 1 in ref. 2) with the aid of a pipette and a small volume of the equilibrated solution. Measure the resin-phase absorbances at 492 nm (the absorption maximum of the bismuth–iodide complex species), $A_{(492)}$, and at 700 nm (in the range where only the resin absorbs light), $A_{(700)}$. The net absorbance of the complex species sorbed on the resin at 492 nm, $A_{RC(492)}$, is obtained from the difference between $A_{(492)}$ and $A_{(700)}$, minus the corresponding difference for the blank. Further procedural details were described previously in this series.[1–3]

To a 1-litre water sample containing 0.022–1.3 μmole of bismuth, add 25 ml of concentrated sulphuric acid, 2.5 g of potassium iodide, 5 ml of 0.1*M* sodium thiosulphate and 0.50 g of Dowex 1-X2 (200–400 mesh) in the sulphate form. Stir the mixture for 30 min and perform the subsequent procedures as mentioned above.

Note 1. When the potassium iodide is added as aqueous solution, the solution should be prepared just before use. Otherwise, a definite value for the absorbance of the resin background cannot be obtained.

Note 2. Iodide is unstable in acidic solution because of aerial oxidation.

Distribution measurements

To a 1-litre water sample containing 75 μmole of bismuth, add 25 ml of concentrated sulphuric acid, 2.5 g of potassium iodide and 0.50 g of Dowex 1-X2 (200–400 mesh) in the sulphate form. Stir the solution till equilibrium is reached (2 hr). Determine the bismuth concentration in the solution separated from the coloured resin beads by the proposed method.

RESULTS AND DISCUSSION

Absorption spectra in the resin and solution

Figure 1 shows the absorption spectrum of the bismuth–iodide complex species sorbed on the anion-exchange resin, compared with those in solution. In

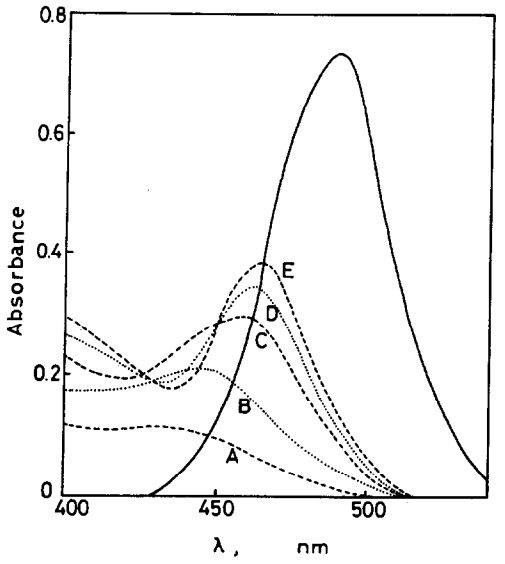

Fig. 1. Absorption spectra of bismuth–iodide complexes. ---, solution spectra. $4 \times 10^{-5}M$ Bi(III), $0.5M$ H_2SO_4; KI, M: A 0.005, B 0.017, C 0.05, D 0.2, E 1; ——, resin spectrum. Resin: Dowex 1-X2 (100–200 mesh, SO_4^{2-} form), 0.50 g. Solution: 1 μmole of Bi(III) in 200 ml + conc. H_2SO_4, 5 ml + KI, 0.5 g.

solution, the absorption maximum is gradually shifted to longer wavelengths with increasing ligand concentration. Eve and Hume[8] have investigated the bismuth–iodide complex system and ascribed the shift to successive complex formation from $[BiI_3]$ to $[BiI_7]^{4-}$ with increase in the iodide concentration from 0.005 to $1.4M$. The spectrum of the resin phase indicates that in spite of the lower ligand concentration in the solution, the absorption maximum is appreciably shifted to longer wavelengths (492 nm) and that complex species with higher ligand numbers are formed. This can be attributed to the effective ligand concentration being higher in an anion-exchange resin than in solution.[9]

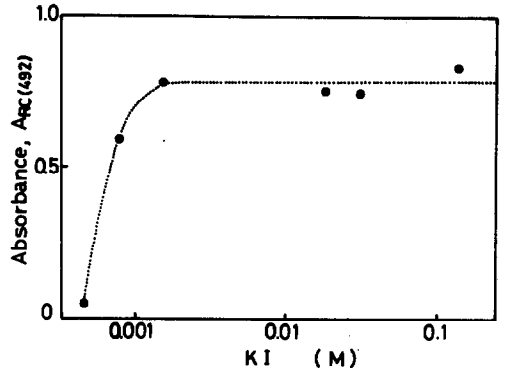

Fig. 2. Variation of absorbance with iodide concentration. Resin: Dowex 1-X2 (100–200 mesh, SO_4^{2-} form), 0.50 g. Solution: 1 μmole of Bi(III) in 200 ml + conc. H_2SO_4, 5 ml + $0.1M$ $Na_2S_2O_3$, 1 ml. Stirring time: 15 min.

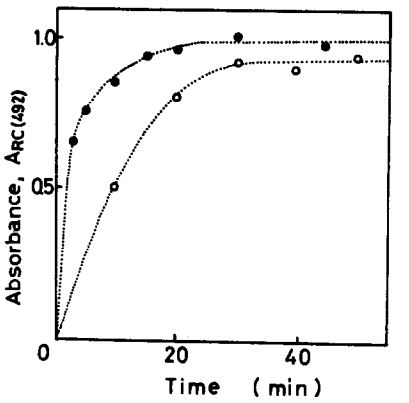

Fig. 3. Time dependence of colour development. ●—Resin; Dowex 1-X2 (100–200 mesh, SO_4^{2-} form), 0.50 g. Solution: 1 μmole of Bi(III) in 200 ml + conc. H_2SO_4, 5 ml + KI, 0.5 g + $0.1M$ $Na_2S_2O_3$, 1 ml. ○—Resin: Dowex 1-X2 (200–400 mesh, SO_4^{2-} form), 0.50 g. Solution: 1 μmole of Bi(III) in 1 litre + conc. H_2SO_4, 25 ml + KI, 2.5 g + $0.1M$ $Na_2S_2O_3$, 5 ml.

Optimization of conditions

Iodide concentration. The absorbances were constant for the potassium iodide concentration range 0.0015–$0.15M$ (Fig. 2). Therefore, 0.25 g of potassium iodide per 100 ml of the sample solution was added, *i.e.*, $1.5 \times 10^{-2}M$ iodide concentration was used.

Sulphuric acid concentration. To prevent hydrolysis of bismuth sulphuric acid was added. No influence on the sorption of the bismuth was observed with variation in sulphuric acid concentration from 0.1 to $1M$. In the standard procedure 2.5 ml of concentrated sulphuric acid was added per 100 ml of sample solution.

Stirring time. The results are shown in Fig. 3. For a 200-ml sample the stirring time was fixed at 10 min, which keeps the operational time reasonably short, at the expense of the sorption equilibrium of bismuth not being reached.

With use of smaller-sized resin beads which have larger surface area, the time dependence of colour development was examined for the l-litre sample system. A reasonable stirring time is 30 min.

For both sample systems the choice of the fixed stirring times is justified by the calibration curves mentioned below.

Calibration and precision

The calibration curves indicate a reasonably linear relationship in the concentration ranges 1.1×10^{-6}–$7.8 \times 10^{-6}M$ for 200-ml samples and 2.2×10^{-8}–$1.3 \times 10^{-6}M$ for 1-litre samples, respectively. The calibration curve for the 1-litre sample system shows that this method is applicable at the ppb (parts per billion) level.

The precision of the method was investigated with series of 10 or 5 determinations for 200-ml and 1-litre samples (Table 1). For the 1-litre samples containing 0.045 μmole of bismuth the relative standard devi-

Table 1. Reproducibility of measurements

Bi(III), M	$A_{RC(492)}$†	Relative standard deviation, %
(1) Sample volume: 200 ml (10 determinations)		
0	0.072 ± 0.005 (A^*)‡	6.4
2.8×10^{-6}	0.429 ± 0.014	3.2
5.6×10^{-6}	0.850 ± 0.015	1.8
(2) Sample volume: 1 litre (5 determinations)		
0	0.127 ± 0.003 (A^*)‡	2.3
4.5×10^{-8}	0.044 ± 0.006	13.0
8.9×10^{-8}	0.083 ± 0.002	2.0

Resin: (1) Dowex 1-X2 (100-200 mesh, SO_4^{2-} form), 0.50 g; (2) Dowex 1-X2 (200–400 mesh, SO_4^{2-} form), 0.50 g.
Solution: (1) 200 ml + conc. H_2SO_4 (5 ml) + KI (0.5 g) + 0.1M $Na_2S_2O_3$ (1 ml); (2) 1 litre + conc. H_2SO_4 (25 ml) + KI (2.5 g) + 0.1M $Na_2S_2O_3$ (5 ml). Stirring time: (1) 10 min, (2) 30 min.
† $A_{RC(492)} = A_{(492)} - A_{(700)} - A^*$.
‡ $A^* = A_{(492)} - A_{(700)}$ (for blank).

ation is larger, but acceptable in view of the low concentration.

Sensitivity

The sensitivity for each system was compared with that of a conventional colorimetric method.[7] The limiting values[1] were $3.3 \times 10^{-6}M$ for 200-ml samples, $5.4 \times 10^{-7}M$ for 1-litre samples, and $7.2 \times 10^{-5}M$ for conventional colorimetry. Ion-exchanger colorimetry in both systems has higher sensitivity than conventional colorimetry.

One of the main advantages of this method is that the sensitivity can be enhanced in proportion as sample volume increases. The increased sensitivity

Table 2. Effects of foreign ions on the determination of bismuth(III)

Added,	molar ratio to Bi	Bi taken $10^{-6}M$	$A_{RC(492)}$	Bi found, $10^{-6}M$	Relative error, %
—	—	3.75	0.826	3.75	0*
Cr(III)	100	3.75	0.799	3.63	−3.2
	1000	3.75	0.846	3·85	+2.7
Fe(III)	100	3.75	0.843	3.83	+2.1
	1000	3.75	0.817	3.71	−1.1
Co(II)	100	3.75	0.859	3.90	+4.0
	1000	3.75	0.851	3.87	+3.2
Pb(II)	100	3.75	0.859	3.90	+4.0
	1000	3.75		Unmeasureable	
—	—	5.57	0.850	5.57	0*
Ni(II)	100	5.57	0.858	5.62	+0.1
	1000	5.57	0.839	5.48	−1.6
Cu(II)	10	5.57	0.833	5.46	−2.0
	100	5.57	0.742	4.86	−12.7
Ag(I)	10	5.57	0.870	5.70	+2.3
	100	5.57		Unmeasureable	
Sn(II)	100	5.57	0.820	5.37	−3.6
	1000	5.57	0.871	5.71	−2.5
NaF	100	5.57	0.858	5.62	+0.9
	1000	5.57	0.843	5.52	−0.9
NaCl	10000	5.57	0.865	5.67	+1.8
	20000	5.57	0.783	5.13	−7.9
	30000	5.57	0.732	4.80	−13.1
NaBr	100	5.57	0.820	5.37	−3.5
	1000	5.57	0.826	5.41	−2.8
$NaNO_3$	100	5.57	0.873	5.72	+2.7
	1000	5.57	0.826	5.41	−2.8
K_2CO_3	100	5.57	0.803	5.26	−5.5
	1000	5.57	0.852	5.58	+0.2
$NaHPO_4$	100	5.57	0.836	5.48	−1.6
	1000	5.57	0.831	5.45	−2.2

* The calibration curves used were not the same, because the different lots of Dowex 1-X2 resin gave different sensitivity.

can be estimated from the distribution ratio, D.[2] For the bismuth–iodide system the value of D was larger than 10^7. The sample volume was changed from 200 ml to 1 litre in this work. The calculated value of the sensitivity ratio for the two sample sizes, $S_{1000/200}$, was 6.1, which is in disagreement with the expected values of 5.0. This can be explained by assuming that the sorption equilibrium for the 200-ml sample solution is less complete.

The relative detection limit is defined as the concentration that produces an absorbance equal to twice the magnitude of the fluctuation in the background absorbance. The values were $6.0 \times 10^{-8} M$ for the 200-ml samples and $6.4 \times 10^{-9} M$ for the 1-litre samples, respectively.

Effect of foreign ions

The effect of foreign ions the determination of bismuth is shown in Table 2. Lead formed a white precipitate of lead sulphate and made measurements impossible when it was present in amount greater than 1000 times that of bismuth. Copper and silver also interfered at 100:1 ratio to bismuth owing to insoluble iodides.

Sodium chloride gave negative errors when present at the level in sea-water. This may indicate that iodide ions were expelled from the anion-exchange resin by chloride ions or that bismuth precipitated as a basic salt such as bismuth oxychloride, BiOCl, so that the concentration of bismuth–iodide complex species in the resin phase decreased. For the determination of bismuth in salt-water it is best to use a calibration curve prepared with standards having the same concentration of sodium chloride as that in the sample solution, or to use the standard addition method.

All the results indicate that minute amounts of bismuth can be determined very selectively without appreciable interference. This method is useful for the determination of bismuth in natural waters and industrial effluents.

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TITRIMETRIC DETERMINATION OF THIOLS: TETRATHIONATE, IRON(III), CYSTINE AND HEXACYANOFERRATE(III) AS THIOL REAGENTS

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Summary—Four analytical reagents, tetrathionate, iron(III), cystine and hexacyanoferrate(III) have been tested with respect to their specificity for oxidation of thiols to disulphides. Of a number of thiols studied, most have a strong tendency to oxidize beyond the disulphide stage with several of the commonly employed reagents. Tetrathionate, cystine and hexacyanoferrate(III) function in phosphate buffer of pH 7, but iron(III) does not require rigid control of pH, although the solution should be only feebly acidic. The reagents were used in excess and the thiosulphate or cysteine formed in the reaction of thiols with tetrathionate or cystine respectively was determined. The residual iron(III) was measured by adding ascorbic acid or mercaptoacetic acid and titrating with 2,6-dichlorophenolindophenol or iodine monochloride respectively; surplus hexacyanoferrate(III) was back-titrated with ascorbic acid. All four reagents react selectively with thiols even in the presence of several possible interfering substances and afford results that are accurate and precise.

The oxidation of thiols is primarily a one-electron change yielding a disulphide:

$$2RSH \rightarrow RSSR + 2H^+ + 2e$$

These compounds can also be oxidized to sulphur(IV) or sulphur(VI) with strong oxidizing agents but such processes are usually more difficult to control and other groups also react. Therefore quantitative procedures based on oxidation beyond the disulphide stage are rare. The use of more than fifty oxidizing agents has been reviewed by Ashworth.[1]

The rapid oxidation with iodine forms a basis for the quantitative determination of thiols,[2] but reports have appeared of the consumption of more than one equivalent of iodine per thiol group. Lucas and King[3] and Larrouquère[4] observed differences in the behaviour of individual thiols, while Simonsen[5] confirmed the importance of concentration with thiols such as cysteine. Danehy *et al.*[6,7] have shown that every thiol has some tendency for over-oxidation, particularly in dilute solutions. Furthermore, β-thiol acids are especially prone to over-oxidation.

Iodine can be employed to determine glutathione[8] and *m*- or *p*-mercaptobenzoic acid but is inapplicable to cysteine, 3- or 4-mercaptobutyric or *o*-mercaptobenzoic acid. Iodate, chloramine-T, hypoiodite, *etc.* have been tried for the determination of mercaptosuccinic acid, but none was suitable.[9] *o*-Iodosobenzoate gives high recoveries if the excess of oxidant is evaluated iodometrically,[10] but this can be obviated by reacting the excess of reagent with ascorbic acid,[11] or titrating thiols directly with the oxidant.[12] 3-Mercaptopropionic and mercaptosuccinic acid could not be determined with *o*-iodosobenzoate.

Copper(II) is suitable for a number of thiols, but it has a strong tendency to form stable complexes without reduction with thiols such as ethylenedithiol, 2-aminobenzenethiol and 8-mercaptoquinoline.[13] Likewise, conditions for the titration of mercaptosuccinic acid with lead tetra-acetate are rigorous and thiols which over-oxidize include cysteine, 2-mercaptoethylammonium chloride and 3-mercaptopropane-1,2-diol.[14]

The reagents which failed on application to thiols "troublesome" to determine by oxidimetry are: *N*-bromosuccinimide,[15,16] phenyl iodosoacetate,[17] periodate,[18] cobalt(III),[19] chloramine-T and -B,[20] *N*-haloamines and *N*-haloamides,[21] inter- and pseudo-interhalogens.[22] These reagents are also not promising in non-aqueous solvents.[23]

In the present work four oxidizing agents, tetrathionate, iron(III), cystine and hexacyanoferrate(III) have been evaluated for their analytical potential. Procedures have been evolved for the rapid and precise determination of several thiols which could not be determined by various available oxidimetric methods.

Tetrathionate

Tetrathionate is a mild oxidizing agent but it has seldom been used for thiol determination. Baernstein[24] determined methionine by demethylation with hydrogen iodide and oxidizing the homocysteine with excess of tetrathionate, the surplus being evaluated with iodate. Anson[25] determined protein thiols by finding the amount of tetrathionate necessary to prevent the appearance of a colour with nitroprusside. That *S*-sulphocysteine is formed in the reaction of cysteine with tetrathionate was established by ion-exchange.[26,27]

It was found in the present work that, although there is apparently no reaction between thiol and tetrathionate in acidic medium, in phosphate buffer of pH 7 the following immediate and quantitative reaction occurs:

$$RSH + S_4O_6^{2-} \rightarrow RS\text{–}S_2O_3^- + S_2O_3^{2-} + H^+$$

The iodimetric titration of the thiosulphate liberated can be used to measure the thiol. It was found in the determination of cysteine, 3-mercaptopropionic and mercaptosuccinic acid that if the liberated thiosulphate was titrated in neutral solution with iodine, the end-point was fleeting, ostensibly because of reaction of the organic product with iodine. When the titration was done in feebly acidic medium, however, the end-point was sharp and stable, and corresponded to reaction with only the released thiosulphate.

Since 0.005*M* iodine is difficult to keep, a solution of iodine monochloride of equivalent strength in dilute hydrochloric acid, which was found to be stable for several months, is used as titrant.

A large number of water-soluble thiols, all showing over-oxidation in reaction with iodine or similar reagents, are determined accurately by the tetrathionate method.

Iron(III)

Coloured products are yielded by many thiols with iron(III).[28] This reagent is found satisfactory for mercaptoacetic acid and cysteine, although less sensitive than nitroprusside.[29]

Thiols have been titrated with iron(III) with nitroprusside as external indicator,[25] or potentiometrically in dimethylformamide[30] or pyridine.[31] The iron(II) formed in the reaction can be estimated colorimetrically by reaction with ferrozine.[32]

Iron(III) oxidizes thiols quantitatively to their disulphides according to the equation

$$2RSH + 2Fe^{3+} \rightarrow RSSR + 2Fe^{2+} + 2H^+$$

The reaction is complete within 1 min. According to the method now evolved, the thiol solution is reacted with an excess of iron(III). The residual iron(III) can be determined by two methods. In the first, an excess of ascorbic acid is added and the surplus ascorbic acid is titrated with 2,6-dichlorophenolindophenol. In the second, an excess of mercaptoacetic acid is added, followed by back-titration with iodine monochloride.

Cystine

Cystine, which has been used for the determination of thiol groups in egg albumin,[25] is undoubtedly the most specific reagent. This reagent, $(CyS)_2$, functions at pH 7, the following reaction taking place:

$$2RSH + (CyS)_2 \rightarrow RSSR + 2CySH$$

The cysteine formed in the reaction is a measure of the thiol present. *o*-Iodosobenzoate, which is an excellent reagent for cysteine, is employed in the proposed method. Thus, the thiol solution in water is reacted with cystine at pH 7. After a minute, the released cysteine is titrated with *o*-iodosobenzoate, with leuco-2,6-dichlorophenolindophenol plus potassium iodide as indicator. At the end-point the vivid blue colour of the oxidized form of the dye is restored.

3-Mercaptopropionic and mercaptosuccinic acid, which could not be determined with *o*-iodosobenzoate,[12] can be determined by treatment with cystine prior to *o*-iodosobenzoate titration.

Hexacyanoferrate(III)

This reagent was first used by Mason[33] and later by Anson,[25,34] and by Mirsky[35] for assaying thiol groups in proteins. At pH 7, thiols are oxidized to disulphides:

$$2RSH + 2[Fe(CN)_6]^{3-} \rightarrow RSSR + 2[Fe(CN)_6]^{4-} + 2H^+$$

Cysteine has been determined by direct titration,[36] or indirectly with the excess of reagent evaluated iodometrically.[37–39] The ferrocyanide produced can be measured colorimetrically[40] or titrated with cerium(IV).[41]

In an attempt to evaluate residual hexacyanoferrate(III) by iodometry the iodine liberated was found to attack the disulphide formed. With mercaptosuccinic acid the results were 3–5% high when about 100% excess of the reagent was used. The cerium(IV) titration[41] seems to give positive errors as cerium(IV) is a powerful oxidant and reacts with disulphides as well as concomitant organic substances. Likewise, the residual hexacyanoferrate(III) cannot be determined with hydrazine sulphate or hydroxylammonium chloride, as these reagents only work in alkaline medium[42] where complications may arise because of alkaline hydrolysis of disulphides to give thiol and sulphinic acid[43] and because hexacyanoferrate(III) is a powerful oxidant in alkaline medium, and oxidation of disulphide or its hydrolysis products is possible.

As a method of accuracy and convenience, the titration of residual hexacyanoferrate(III) in phosphate buffer of pH 7 with ascorbic acid, with 2,6-dichlorophenolindophenol as indicator, is used in the present work. The surplus reagent can also be determined by reaction with excess of mercaptoacetic acid and back-titration of the surplus with iodine monochloride. However, the first method is more direct.

EXPERIMENTAL

Reagents

Sodium tetrathionate solution, 0.025M. Prepared by dissolving 6.75 g in 1 litre of water. This solution should show no trace of turbidity and no iodine uptake. The following method is recommended for preparing fresh solutions of tetrathionate.

Titrate 100 ml of 0.1*M* sodium thiosulphate with 0.05*M* iodine to the first appearance of the iodine colour and add 0.2 ml more. Shake for 5 min and bleach the excess of iodine by dropwise addition of 0.01*M* thiosulphate solution. Purge the reagent solution with nitrogen and store in a stoppered dark-coloured bottle.

Iron(III) sulphate solution, 0.01M. Prepared by oxidizing 3.92 g of ammonium iron(II) sulphate with 2–3 g of potassium peroxodisulphate and boiling to decompose the latter. The red colour of iron(III) hydroxide formed by hydrolysis is removed by dropwise addition of dilute sulphuric acid. The solution is finally diluted to 1 litre. It is standardized as follows. A 5-ml portion is treated with 10 ml of 0.005*M* ascorbic acid and swirled for 1 min, then 1 ml of glacial acetic acid is added and the residual ascorbic acid titrated with 0.0025*M* 2,6-di-chlorophenolindophenol to a pink colour. A blank is run on the same volume of ascorbic acid.

Cystine hydrochloride solution, 0.02M. Prepared by treating 4.80 g of reagent grade cystine with 12 ml of 5*M* hydrochloric acid in a 250-ml beaker. The mixture is agitated with a glass rod and the resulting salt dissolved in water added 3–4 ml at a time and stirred well, then diluted to 1 litre. This solution should show no consumption of *o*-iodosobenzoate.

Hexacyanoferrate(III) solution, 0.05M. This solution (16.5 g of reagent grade material per litre) is standardized by taking 5 ml of it, adding 5 ml of phosphate buffer of pH 7, 15 ml of water and 1 ml of 0.025% 2,6-dichlorophenolindophenol indicator, and titrating with 0.02*M* ascorbic acid till the indicator is bleached. An indicator blank is also determined.

Potassium o-iodosobenzoate solution, 0.005M. Prepared by dissolving 1.325 g of the free acid in a slight excess of 0.1*M* potassium hydroxide and diluting to 1 litre, and standardized iodimetrically.[10]

Iodine monochloride solution, 0.005M. Prepared by dissolving 0.357 g of potassium iodate and 0.550 g of potassium iodide in 200 ml of water, adding about 50 ml of concentrated hydrochloric acid in a single lot, shaking the mixture for 5 min, and diluting to 1 litre. One ml of carbon tetrachloride is added and the solution is shaken vigorously. Any violet colour in the organic layer is bleached by addition of 0.002*M* iodate. Otherwise 0.01*M* potassium iodide is added until a faint violet colour appears in the carbon tetrachloride. The solution is then standardized iodimetrically.

2,6-Dichlorophenolindophenol solution, 0.0025M. Prepared by stirring together 0.73 g of the sodium salt of the indicator and 0.2 g of sodium carbonate in 500 ml of water for 30 min and filtering off the insoluble portion. The filtrate is diluted to 1 litre and standardized against analytical grade ascorbic acid.[44] This solution is stable for 4 days if stored in the dark at 20°.

Ascorbic acid solution, 0.02M. Prepared by dissolving 3.522 g in 1 litre of water and standardized against iodate. A 0.005*M* solution is made by diluting the stock solution.

Mercaptoacetic acid solution, 0.01M. Prepared by dissolving an approximate volume of the pure substance in water and standardized iodimetrically.[2]

Leuco-2,6-dichlorophenolindophenol solution. Prepared by adding 5 ml of phosphate buffer of pH 7 to 20 ml of 0.05% solution of the sodium salt of the oxidized form of the indicator and bleaching the blue colour by dropwise addition of 0.005*M* ascorbic acid. The reduced indicator oxidizes when exposed to the air and this necessitates decolorization before each use.

Phosphate buffer, pH 7. Made by dissolving 117.7 g of dipotassium hydrogen orthophosphate and 44.1 g of potassium dihydrogen orthophosphate in 1 litre of water.

Procedures

Determination with tetrathionate. To the sample solution, containing 0.1–0.3 mmole of thiol, add 5 ml of phosphate buffer and 10 ml of 0.025*M* tetrathionate. Swirl the solution for 1 min. Add 0.5 g of potassium iodide, 1 ml of 0.5% starch solution, 25 ml of water and 3 ml of 0.1*M* hydrochloric acid. Titrate the liberated thiosulphate with 0.005*M* iodine monochloride to the appearance of a blue colour.

Determinations with iron(III). Procedure A: take the sample solution in water, methonol, acetonitrile or dimethylformamide, containing 0.02–0.1 mmole of thiol, and treat it with about 50% excess of 0.01*M* iron(III). Swirl it for about 1 min, add a measured excess of 0.005*M* ascorbic acid and 1 ml of glacial acetic acid, and titrate with 0.0025*M* 2,6-dichlorophenolindophenol to a pink colour. Run a blank determination.

Alternatively, (procedure B) treat the sample solution, containing 0.05–0.15 mmole of thiol, with 20 ml of 0.01*M* iron(III). Allow to react for about 1 min and add 25 ml of 0.01*M* mercaptoacetic acid. Again swirl for 1 min; add 3 ml of 0.1*M* hydrochloric acid, 0.5 g of potassium iodide and 1 ml of 0.5% starch, and titrate with 0.005*M* iodine monochloride to the appearance of a blue colour. Run a blank determination.

Determination with cystine. To the aqueous sample solution, containing 0.03–0.1 mmole of thiol, add 5 ml of phosphate buffer and 15 ml of 0.02*M* cystine hydrochloride, and swirl for 1 min. Add 1 ml of leuco-2,6-dichlorophenolindophenol indicator plus about 20 mg of potassium iodide. Titrate with 0.005*M* *o*-iodosobenzoate. The titration should be done slowly (10 ml of titrant added during a period of 2 min) and near the end-point the addition of each drop of titrant is followed by swirling for 10 sec; at the end-point the vivid blue colour of the oxidized form of the indicator appears.

Determination with hexacyanoferrate(III). To the aqueous sample solution, containing 0.3–0.5 mmole of thiol, add 5 ml of phosphate buffer, 15 ml of 0.05*M* hexacyanoferrate(III) and swirl for 1 min. Thereafter, add 1 ml of 0.0025*M* sodium 2,6-dichlorophenolindophenol indicator and titrate the residual hexacyanoferrate(III) with 0.02*M* ascorbic acid. At the end-point the blue colour of the indicator is bleached. Run a blank determination on the same volumes of hexacyanoferrate(III) and indicator.

RESULTS AND DISCUSSION

Results for the determination of thiols with tetrathionate are given in Table 1. All of the thiols tested showed over-oxidation in their reaction with iodine or allied reagents but a stoichiometric reaction was observed with tetrathionate.

Iron(III) forms disulphides with a large number of thiols (Table 2). In procedure A, glutathione underwent only 20–30% oxidation, presumably because of its ability to form a complex with iron(III). With alkanethiols, there was only 10–15% reaction; groups such as carboxyl, amino or hydroxyl on the alkyl chain appear to activate the thiol function for ready oxidation. In procedure B, the unreacted glutathione or lower alkanethiols reacted with iodine monochloride in the back-titration, therefore, the thiol recovery agreed with the theoretical. However, the end-point is only fleeting when 1-dodecanethiol, which reacts slowly with iodine monochloride, is determined, indicating thereby an incomplete reaction with iron(III).

The alkanethiols were not determined with the other three reagents, mainly because of their low solubility in aqueous medium.

In Table 3, results obtained with cystine and hexacyanoferrate(III) are presented. Cystine is particularly suited for determining thiol groups in biological

Table 1. Determination of thiols with tetrathionate

Thiol	Purity, % Proposed method[a] Range	Average	Standard deviation	Comparison method
Cysteine	99.6–99.9	99.8	0.10	99.7[b]
Homocysteine	97.4–97.6	97.5	0.11	97.6[b]
Glutathione	98.0–98.3	98.2	0.08	98.0[b]
N-Acetylhomocysteine	97.8–98.1	97.9	0.12	98.1[b]
N-Methylcysteine	98.5–98.7	98.6	0.15	98.9[c]
3-Mercaptopropionic acid	96.0–96.4	96.2	0.20	96.3[d]
Mercaptosuccinic acid	98.0–98.5	98.2	0.18	98.4[c]
N-Isopropylcysteine	98.8–99.2	99.0	0.08	99.3[c]
N-Phenylcysteine	98.1–98.5	98.3	0.20	98.5[c]
3-Mercaptobutyric acid	99.8–100.1	99.9	0.15	100.1[f]
Mercaptomethylsuccinic acid	98.1–98.6	98.4	0.18	98.6[f]
4-Mercaptobutyric acid	97.7–98.3	97.9	0.13	98.2[f]

[a] Eight determinations; [b] *o*-Hydroxymercuribenzoate[45]; [c] *N*-Bromosuccinimide[46]; [d] Lead tetra-acetate[14]; [e] *o*-Hydroxymercuribenzoate[47]; [f] Mercury(II) perchlorate[48].

Table 2. Determination of thiols with iron(III)

Thiol	Purity, % Method A[a]	Standard deviation	Method B[a]	Standard deviation	Comparison method
Cysteine	99.7	0.1_2	99.8	0.1_0	99.6[b]
N-Propylcysteine	98.5	0.2_1	98.4	0.1_6	98.4[c]
Homocysteine	97.6	0.1_3	97.4	0.1_1	97.6[d]
3-Mercaptopropionic acid	93.1	0.1_5	96.0	0.1_6	96.3[e]
Mercaptosuccinic acid	98.3	0.2_1	98.5	0.1_9	98.4[d]
2-Mercaptobenzoic acid	99.8	0.1_8	99.6	0.1_5	99.7[e]
3-Mercaptopropane-1,2-diol	79.6	0.1_0	79.4	0.1_1	79.5[f]
2-Mercaptoethanol	98.8	0.1_0	98.9	0.1_0	99.1[g]
2-Diethylaminoethanethiol	98.2	0.1_1	98.0	0.1_0	98.4[f]
2-Mercaptoethylammonium chloride	98.3	0.1_4	97.8	0.1_0	98.1[f]
Benzenethiol	99.3	0.2_0	99.7	0.1_2	99.5[e]
2-Naphthalenethiol	98.2	0.1_8	97.8	0.1_3	98.0[h]
4-Mercaptobutyric acid	98.0	0.2_3	98.3	0.1_6	98.5[g]
4-Chlorobenzenethiol	99.5	0.1_0	99.7	0.1_5	99.8[h]
4-*t*-Butylbenzenethiol	99.4	0.1_5	99.5	0.1_4	99.6[e]
2,5-Dimercaptoadipic acid	98.5	0.2_2	99.5	0.1_9	98.7[f]

[a] Eight determinations; [b] Mercury(II) chloride[49]; [c] *N*-Bromosuccinimide[46]; [d] *o*-Hydroxymercuribenzoate[47]; [e] Lead tetra-acetate[14]; [f] *o*-Iodosobenzoate[12]; [g] Copper(II) sulphate[19]; [h] Sodium methoxide[50].

Table 3. Determination of thiols with cystine and hexacyanoferrate(III)

Thiol	Purity, % Proposed method[a] Range	Average	Standard deviation	Comparison method
With cystine				
3-Mercaptopropionic acid	96.0–96.5	96.4	0.1_9	96.3[b]
Mercaptosuccinic acid	98.1–98.6	98.5	0.2_2	98.4[c]
Mercaptomethylsuccinic acid	98.2–98.8	98.5	0.1_6	98.6[d]
3-Mercaptobutyric acid	99.6–99.9	99.8	0.1_8	100.1[d]
With hexacyanoferrate(III)				
N-Butylcysteine	98.4–98.9	98.7	0.1_1	98.7[e]
Homocysteine	97.3–97.6	97.4	0.1_3	97.6[e]
3-Mercaptobutyric acid	99.4–99.8	99.7	0.1_0	100.1[d]
Mercaptomethylsuccinic acid	98.1–98.7	98.5	0.1_0	98.6[d]
4-Mercaptobutyric acid	97.9–98.3	98.1	0.1_6	98.2[d]
3-Mercaptopropane-1,2-diol	79.0–79.6	79.4	0.1_0	79.5[f]
Glutathione	97.7–98.3	98.0	0.1_1	98.1[g]

[a] Eight determinations; [b] Lead tetra-acetate[14]; [c] *o*-Hydroxymercuribenzoate[47]; [d] Mercury(II) perchlorate[48]; [e] *N*-Bromosuccinimide[46]; [f] *o*-Iodosobenzoate[12]; [g] Chloramine-T[51].

Table 4. Interferences

Thiol	Compound added	Moles of compd. added per mole of thiol	Thiol recovery* % A	B	C	D
3-Mercaptopropionic acid	Methionine	55	100.0	99.9	99.9	100.1
	Tyrosine	20	99.9	100.3	100.2	100.0
	Tryptophan	35	100.1	100.5	100.2	100.2
	Cystine	62	100.0	99.9	—	99.9
Cysteine	Glycine	130	99.9	100.1	100.0	100.0
	Serine	168	100.0	99.9	99.9	100.0
3-Mercaptopropane-1,2-diol	Thiophene	15	100.1	100.8	100.2	100.3
	Diethylsulphone	33	99.8	99.7	99.8	99.6
	Glucose	48	99.9	100.2	100.0	100.2
	Urea	69	100.0	100.1	99.8	100.0
2-Mercaptoethanol	Biotin	21	100.0	100.4	100.0	100.2
	Acrylonitrile	136	99.2	99.5	99.0	99.2
	Lanthionine	50	99.9	100.3	99.9	100.4
	Maleic acid	122	99.8	100.0	99.9	99.8
	Allyl alcohol	86	99.9	99.7	99.7	99.8
3-Mercaptobutyric acid	Diphenyldisulphide	25	100.0	100.0	99.9	100.0
	Acrylamide	144	99.6	99.8	99.5	99.5
	Dimethylsulphoxide	51	100.0	99.8	100.0	99.9

* Average of 3 determinations, % recovery takes into account the previously determined purity of thiol; A, tetrathionate; B, iron(III); C, cystine; D, hexacyanoferrate(III).

materials as it does not oxidize any other group in the protein molecule. The titration of the released cysteine with *o*-iodosobenzoate must be done slowly, as fast titrations result in high recovery. Clearly, the reaction of *o*-iodosobenzoate with cysteine is quick but that with iodide is slow; it is the iodine formed intermediately which oxidizes leuco-indophenol to the blue dye.

Hexacyanoferrate(III) is among the reagents that have been used extensively for thiol determinations. As with iron(III), a blank determination is needed.

No particular excess of cystine or tetrathionate is needed, even a three-fold excess having no adverse effect. Similarly, no over-oxidation was evident when about 200% excess of iron(III) or hexacyanoferrate(III) was employed.

Although all four reagents gave accurate and precise results on application to several thiols, tetrathionate is advocated as the best reagent for water-soluble thiols, largely on account of its easy preparation, low cost, rapid and selective action even in the presence of substances that interfere in one or another of the other methods, convenient titrimetric finish and the fact that no blank determination is required.

For water-insoluble but reactive thiols, iron(III) seems to be a promising reagent. The second procedure is especially convenient because of the good stability of the reagents.

In Table 4, results for the determination of thiols in the presence of several interfering compounds are given. The interferences studied included compounds that interfere in existing methods, and compounds possessing other sulphur-containing functional groups. Iodide interferes with the iron(III) and hexacyanoferrate(III) procedures, and sulphide, sulphite, thiosulphate, thiourea and ascorbic acid vitiate determinations with all four reagents.

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A SPECTROPHOTOMETRIC DETERMINATION OF 1-NAPHTHOL IN DECIMILLIGRAM AMOUNTS

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Summary—1-Naphthol is determined by spectrophotometric measurement at 510 nm after oxidation with vanadium(V) in ~4*M* hydrochloric acid and extraction of the oxidation product into toluene.

Very few methods are available for the selective determination of 1-naphthol. Sodium cuprobromide has been used for the colorimetric determination of 1-naphthol in the presence of 2-naphthol in the microgram range,[1] but the colour fades after about 5 min. Another method is based on the fact that 1-naphthol is diazotized faster than 2-naphthol.[2] In the present report we summarize our studies on the development of a new method for the spectrophotometric determination of 1-naphthol in the presence of 2-naphthol and other phenols. A stable violet colour extractable into toluene is formed by the reaction of 1-naphthol with ammonium vanadate in presence of hydrochloric acid.

EXPERIMENTAL

Reagents

Ammonium vanadate solution, 2%.

1-Naphthol solution. A 1% solution freshly prepared in alcohol and diluted as required.

Procedure

Transfer 1 ml of sample containing 20–600 μg of 1-naphthol to a boiling-tube. Add 1 ml of 2% ammonium vanadate solution and 0.5 ml of concentrated hydrochloric acid. Heat on a water-bath at 60 ± 2° for 5 min. Cool, extract with 10 ml of toluene and then measure the absorbance at 510 nm against a blank treated similarly. Prepare a calibration curve by applying the procedure to 1-ml portions of 20–600 μg/ml standard solutions.

RESULTS

For the determination of 1-naphthol the optimum conditions were investigated as follows. The redox reaction between 1-naphthol and vanadium(V) depends mainly on the temperature, the ammonium vanadate concentration, and the concentration of hydrochloric acid. To study the effects of these variables, 1 ml of 0.02% 1-naphthol solution was treated according to the procedure with two of the factors kept constant and the third varied. The results are given in Table 1. The effect of the volume of hydrochloric acid used was similarly studied: the absorbances were 0.25, 0.33, 0.36, 0.36, 0.37, 0.37, 0.36 and 0.35 for 0.05, 0.1, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0 ml of the concentrated acid.

Interferences

1-Naphthol was determined in presence of various compounds. The results are summarized in Table 2. It was observed that methanol, diethyl ether, bromobenzene, acetamide, benzamide, nitrobenzene, *m*-dinitrobenzene, glucose, methyl n-propyl ketone, benzonitrile and benzoic acid, present in hundredfold amount relative to the naphthol, do not affect the absorbance.

Other phenols do not interfere up to a certain limit, *e.g.*, 300 μg of 1-naphthol can be determined in the presence of phenol (1.5 mg), picric acid (1.4 mg), *o*-nitrophenol (1.0 mg), 2-naphthol (3.0 mg), 8-hy-

Table 1. A study of optimum conditions for the colour reaction of 1-naphthol and ammonium vanadate

Temperature varied		Vanadate varied		Acid varied	
Temperature. °C	Absorbance	[V], %	Absorbance	[HCl], *M*	Absorbance
25 ± 1	0.23	2.0	0.38	11.6	0.37
40 ± 1	0.28	1.0	0.37	9.0	0.33
50 ± 2	0.35				
60 ± 2	0.38	0.5	0.38	8.0	0.31
65 ± 2	0.38				
70 ± 2	0.36	0.25	0.35	4.0	0.23
80 ± 2	0.34	0.125	0.28	1.0	0.20
98 ± 2	0.18	0.062	0.17	0.10	0.10

Table 2. Determination of 1-naphthol (300 μg) in the presence of other organic compounds

Organic compound added as impurity	Added, mg	1-Naphthol found, μg	Error, %
o-Nitrophenol	1.0	310	+3.3
p-Nitrophenol	1.2	310	+3.3
Picric acid	1.5	300	0
Vanillin	3.0	300	0
Phenol	1.0	315	+5
2-Naphthol	3.0	300	0
8-Hydroxyquinoline	0.5	295	−1.6
Phloroglucinol	0.6	305	+1.6
Quinol	2.5	310	+3.3
m-Cresol	4.0	295	−1.6
Acetamide	100	305	+1.8
Benzamide	300	305	+1.6
Acetic acid	110	315	+5
m-Dinitrobenzene	100	300	0
Methyl n-propyl ketone	90	300	0
Benzonitrile	100	315	+5
Glucose	100	305	+1.6
Formaldehyde*	125	310	+3.3
Acetaldehyde*	390	305	+1.6
Methylamine*	125	300	0

* Sample solution heated on a water-bath for 15 min at 100°.

droxyquinoline (0.5 mg), phloroglucinol (0.3 mg), catechol (2.5 mg), resorcinol (1.0 mg), vanillin (3.0 mg) *m*-cresol (4.0 mg) and quinol (2.5 mg).

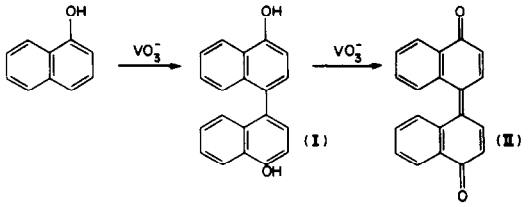
Interference by low-boiling aldehydes and amines can be removed simply by boiling the sample solution for 15 min.

Beer's law is obeyed for 20–600 μg of 1-naphthol.

The reproducibility of the results was checked with six replicate determinations of 400 μg of 1-naphthol. The standard deviation was 10 μg. The accuracy of the method was checked by analysis of four unknowns. The average error was 1.4%.

DISCUSSION

The results reveal that the reaction can be used for a fairly selective and sensitive determination of 1-naphthol. The reaction is most sensitive when conducted at 60–65°. It was found that 1 ml of 0.5% ammonium vanadate solution is sufficient for colour development with 200 μg of 1-naphthol and a bigger volume does not cause any appreciable change; hence 1 ml of 2% vanadate solution should suffice for 800 μg of 1-naphthol but the calibration curve is linear only up to 600 μg. The hydrochloric acid concentration is important, the concentrated acid being best, but the volume used is not critical. The product can be extracted into toluene and the interference of a number of compounds is removed in this way. The colour is stable for up to an hour and this is a distinct advantage over the method of Sass *et al.* The probable mechanism is oxidation of 1-naphthol to compound **II** through 4,4'-di-1-naphthol (**I**) as intermediate:



Support of this mechanism is obtained from the work of Edwards and Cashaw[3] who obtained a bluish-violet compound (**II**) by the oxidation of 4,4'-di-1-naphthol (**I**) with lead tetra-acetate. This product gave no melting point (a characteristic of many quinones) and its analysis is in approximate agreement with the values for (**II**): calc. for $C_{20}H_{12}O_2$, C 84.4%, H 4.2%; found C 83.5%, H 4.1%. Our product also gave no melting point. On reduction with sodium bisulphite (**II**) gives the colourless product (**I**), in agreement with the studies of Edwards and Cashaw.[3]

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COMPARISON OF EXPERIMENTAL AND CALCULATED RELATIVE SENSITIVITY COEFFICIENTS FOR SPARK-SOURCE MASS-SPECTROMETRY OF METALS

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Summary—Sensitivity calibration has been performed for the spark-source mass-spectrometric analysis of iron, copper and aluminium matrices, with standard reference materials. The experimental relative sensitivity coefficients, corrected for discrimination effects in the mass spectrometer, are compared with values obtained with various empirical approaches to calculate relative sensitivity coefficients for an r.f. spark. The best correlation found is only of the order of 50%.

Accurate spark-source mass-spectrometric analysis requires calibration with standard reference materials. Relative sensitivity coefficients, S_R, have been determined for a number of elements in an iron, copper and aluminium matrix with photographic and electrical detection and results reported.[1–4] After correction for discrimination effects in the mass spectrometer, there is a fair agreement between the relative sensitivity coefficients obtained with both methods of detection.[5] The results obtained with electrical detection in the peak-switching mode were more precise than the others and were therefore used exclusively for the comparison with calculated values.

Several empirical approaches can be found in the literature for estimating relative sensitivities of elements in an r.f. spark from physical parameters of the element (x), the internal standard (y) and in some cases the matrix (z). They are summarized in Table 1. Methods which cannot be compared with our experimental results because they are extrapolations of measured values, (*e.g.*, McCrea[18] and Taylor[19]), or because they apply to compounds, (*e.g.*, Konishi[20] and Oblas[21]), are not included in the Table. The physical parameters used to calculate the relative sensitivity coefficients are listed in Table 2.

The use of calculated sensitivity coefficients in spark-source mass-spectrometry may be useful when no reference materials are available for straightforward calibration. The comparison of the calculated and experimentally determined relative sensitivity coefficients gives an idea of the accuracy that can be expected in this situation.

EXPERIMENTAL

The instrument used was a double-focusing mass spectrometer (JMS-01-BM-2, JEOL, Tokyo), incorporating a spherical electric sector. Electrical detection is used in the magnetic peak-switching mode.

The standard reference materials used were four low-alloy steels (SRM 661–664), one electrolytic iron (SRM 665) and five copper-base alloys (SRM 1101, 1102, 1106, 1108 and 1121) all from NBS, Washington, D.C., four copper rods (SSC 1–4) from the Canada Centre for Mineral and Energy Technology, Ottawa, three copper samples containing standardized platinum contents from the BCR, Brussels, eight dilute copper alloys (CA 3, 4, 6; CB 0, 1; CC 1, 3, 5) and five aluminium samples (AA 1–5) from Johnson Matthey Ltd., London, and ten samples from Aluminium Pechiney representing three types of alloy: Al–Si–Cu, Al–Cu and Al–Mn. Their chemical composition has been described in detail elsewhere.[1,3,4]

The sparking conditions for the iron and steel samples were: spark-source voltage 60 kV, pulse length 20 μsec, repetition frequency 3000/sec. For the copper and aluminium samples they were 40 kV, 20 μsec, 3000/sec and 30 kV, 20 μsec, 1000/sec, respectively.

The width of the slits was chosen as follows: object slit 100 μm, α-slit and β-slit 2.0 mm. The energy-defining (β) slit was chosen to be wide enough to avoid discrimination effects in the electrostatic analyser.[5] The collector slit was 250 μm for the iron samples, 350 μm for the copper samples and 1200 μm for the aluminium samples.

RESULTS AND DISCUSSION

The various equations in Table 1 contain only parameters relating to ion-production in the source. Hence, before comparison of the calculated sensitivity coefficients with experimental values, the latter must be corrected for the influence of phenomena occurring after ion-production. Discrimination between ions may occur during ion-extraction from the source, ion-energy selection at the β-slit, transmission through the analyser, and finally, detection of the ions. It can also arise from the influence of the collector slit setting. The influence of all these effects has been studied for the iron samples.[5] The corrected experimental values are listed in the last column of Table 3, together with values calculated by using the various approaches from Table 1. The ratio between the calculated and experimental coefficients is indicated in Table 4. The best agreement is obtained with the equations proposed by Goshgarian and Jensen[10,11] and

Table 1. Calculation of sensitivity coefficients

Authors	Proposed equation
Addink[6,7]	$\Delta T = T_z - T_x = -2500 \log[S_R(x/y)_z]^{-1}$ $S_R(x/y)_z = 1$ when $T_x > T_z$
Kai, Miki[8,9]	$S_R(x/y)_z = \frac{(\Delta H)_x}{(\Delta H)_z} \cdot \frac{\phi_x}{\phi_z}$
Goshgarian, Jensen[10,11]	$S_R(x/y)_z = \frac{(\Delta H)_x}{(\Delta H)_z} \cdot \frac{(CR)_x^2}{(CR)_z^2} \cdot \frac{\phi_x}{\phi_z}$
Honig[12]	$S_R(x/y)_z = \frac{(\Delta H)_x}{(\Delta H)_z} \cdot \frac{Q_x}{Q_z}$
Ménétrier[13]	$S_R(x/y)_z = \frac{(\Delta H)_x}{(\Delta H)_z} \cdot \frac{(CR)_x^2}{(CR)_z^2}$
Willardson, Socha[14]	$S_R(x/y)_z = \left(\frac{\phi_x}{\phi_z}\right)^{3.3}$ when $\phi_x < \phi_z$
Vidal, Galmard, Lanusse[15–17]	$S_R(x/y)_z = \frac{(\Delta H)_x}{(\Delta H)_z} \cdot \frac{Q_x}{Q_z} \cdot \left(\frac{\phi_x}{\phi_z}\right)^4$

by Willardson and Socha[14] for which the average deviation is a factor of 1.48. If no sensitivity coefficients are used, *i.e.*, if all coefficients are set equal to 1, this factor becomes 2.20.

It can be noticed that for a number of elements, all calculated values are lower than the experimental values, *e.g.*, by a factor of 1.30–2.23 for Mn, 1.33–2.05 for Cu, 1.92–3.39 for Sn and 1.43–3.60 for Sb. This could be caused by the energy conditions that are needed to spark iron and steel samples. Indeed, it was shown earlier that for elements with boiling and melting points considerably lower than those of iron (used as internal standard), the experimental sensitivity coefficients increase with more energetic sparking conditions.[22] This line of argument does not hold for copper which has boiling and melting points comparable with those of iron. The high experimental sensitivity coefficient of copper in iron samples compared to that in other matrices was also obtained by other authors.[12,16,23]

The corresponding results for the copper matrix are listed in Table 5. The experimental sensitivity coefficients are also corrected for discrimination effects after ion-production. Most of the equations used to calculate the sensitivity coefficients contain only parameters of the element to be determined and of the internal standard. Hence, the calculated coefficients are independent of the matrix. Exceptions are the equations proposed by Addink,[6,7] where the difference in boiling point between element and matrix is used, and by Willardson and Socha,[14] where the ionization potential of the element must be lower than that of the matrix. When the ratio of the calculated and experimental coefficients is used, (as for the iron matrix in Table 4), the best results are obtained with the equations proposed by Goshgarian and Jensen[10,11] and by Kai and Miki,[8,9] for which the average deviation of the calculated coefficients from the experimental values is by a factor of 1.50. If all sensitivity coefficients are set equal to 1, this factor becomes 1.78.

In the case of the aluminium matrix, the equation proposed by Willardson and Socha cannot be applied, because the first ionization potential of the matrix element is lower than those of all determined elements. The calculated sensitivity coefficients are compared with the experimental values in Table 6. The calculated values show an average deviation by a factor of 1.40 from the experimental values for the equations proposed by Kai and Miki,[8,9] Goshgarian and

Table 2. Physical parameters used for the calculation of relative sensitivity coefficients

Symbol	Meaning	Source
T	Boiling point	*Handbook of Chemistry and Physics*, ed. R. C. Weast, CRC Press, Cleveland, Ohio, 1974–75.
ΔH	Heat of sublimation at 298 K	O. Kubaschewski, E. Ll. Evans and C. B. Alcock, *Metallurgical Thermochemistry*, Pergamon, Oxford, 1967.
ϕ	First ionization potential	*Handbook of Chemistry and Physics*, ed. R. C. Weast, CRC Press, Cleveland, Ohio, 1974–75.
CR	Covalent radius	Landolt-Börnstein, 6 Aufl., Bd. 4, p. 529, Springer Verlag, Berlin, 1955.
Q	Ionization cross-section	J. W. Otvos and D. P. Stevenson, *J. Am. Chem. Soc.*, 1956, **78**, 547.

Table 3. Calculated and experimental sensitivity coefficients for iron and steel samples (Fe: $S_R = 1$)

Element	Calculated S_R-value							Experimental S_R-value
	Addink	Kai, Miki	Goshgarian, Jensen	Honig	Ménétrier	Willardson, Socha	Vidal *et al.*	
Ti	1	0.98	1.28	1.12	1.10	1.60	1.98	2.0 ± 0.2
V	1	0.91	1.03	0.97	0.88	1.67	1.79	1.6 ± 0.2
Cr	1.07	1.17	1.21	1.01	1.04	1.65	1.85	1.7 ± 0.1
Mn	2.07	1.50	1.57	1.53	1.49	1.21	1.92	2.7 ± 0.2
Co	1	0.94	0.90	0.87	0.89	1.00	0.88	0.86 ± 0.09
Ni	1.02	0.96	0.96	0.81	0.93	1.11	0.91	0.84 ± 0.08
Cu	1.18	1.20	1.18	0.78	1.16	1.06	0.84	1.6 ± 0.2
As	7.16	2.63	3.52	2.19	4.39	*	0.91	3.0 ± 0.4
Zr	1	0.75	1.17	1.39	1.01	1.59	2.44	2.0 ± 0.2
Nb	1	0.63	0.83	1.13	0.73	1.56	1.94	1.6 ± 0.2
Mo	1	0.67	0.80	1.12	0.72	1.40	1.70	1.2 ± 0.1
Sn	1.56	1.40	2.14	1.21	2.00	1.26	1.52	4.1 ± 0.8
Sb	2.51	1.42	2.25	1.46	2.48	*	1.00	3.6 ± 0.6
La	1	1.32	2.79	†	1.99	3.06	†	5 ± 1
Ta	1	0.51	0.68	†	0.68	*	†	0.9 ± 0.1
W	1	0.46	0.56	†	0.56	*	†	0.6 ± 0.1

* $\phi_x > \phi_r$.
† Q unknown.

Jensen,[10,11] Honig[12] and Ménétrier.[13] For sensitivity coefficients equal to 1 the average deviation is 1.78.

CONCLUSIONS

The best correlation between calculated sensitivity coefficients based on various semi-empirical equations found in the literature and our experimental values, corrected for discrimination effects occurring in the mass spectrometer, is found with the equation proposed by Goshgarian and Jensen. Even in this most favourable case there remains an average deviation of 40–50%.

Hence for accurate work, the use of one or more reference materials remains mandatory. Nevertheless it appears that, if no reference materials are available for the analysis of metal samples, it is better to use calculated sensitivity coefficients than to apply no correction at all to the data.

To obtain better results with calculated sensitivity coefficients, it is felt that the equations should not only contain physical parameters relating to the im-

Table 4. Ratio of the calculated and experimental sensitivity coefficients for iron and steel samples

Element	Addink	Kai, Miki	Goshgarian, Jensen	Honig	Ménétrier	Willardson, Socha	Vidal *et al.*
Ti	2.00^{-1}	2.04^{-1}	1.56^{-1}	1.79^{-1}	1.82^{-1}	1.25^{-1}	1.01^{-1}
V	1.60^{-1}	1.76^{-1}	1.55^{-1}	1.65^{-1}	1.82^{-1}	1.04	1.12
Cr	1.59^{-1}	1.45^{-1}	1.40^{-1}	1.68^{-1}	1.63^{-1}	1.03^{-1}	1.09
Mn	1.30^{-1}	1.80^{-1}	1.72^{-1}	1.76^{-1}	1.81^{-1}	2.23^{-1}	1.41^{-1}
Co	1.16	1.09	1.05	1.01	1.03	1.16	1.02
Ni	1.21	1.14	1.14	1.04^{-1}	1.11	1.32	1.08
Cu	1.36^{-1}	1.33^{-1}	1.36^{-1}	2.05^{-1}	1.38^{-1}	1.51^{-1}	1.90^{-1}
As	2.39	1.14^{-1}	1.17	1.37^{-1}	1.46	—	3.30^{-1}
Zr	2.00^{-1}	2.67^{-1}	1.71^{-1}	1.44^{-1}	1.98^{-1}	1.26^{-1}	1.22
Nb	1.60^{-1}	2.54^{-1}	1.93^{-1}	1.42^{-1}	2.19^{-1}	1.03^{-1}	1.21
Mo	1.20^{-1}	1.79^{-1}	1.50^{-1}	1.07^{-1}	1.67^{-1}	1.17	1.42
Sn	2.63^{-1}	2.93^{-1}	1.92^{-1}	3.39^{-1}	2.05^{-1}	3.25^{-1}	2.70^{-1}
Sb	1.43^{-1}	2.54^{-1}	1.60^{-1}	2.47^{-1}	1.45^{-1}	—	3.60^{-1}
La	5.00^{-1}	3.79^{-1}	1.79^{-1}	—	2.51^{-1}	1.63^{-1}	—
Ta	1.11	1.76^{-1}	1.32^{-1}	—	1.32^{-1}	—	—
W	1.67	1.30^{-1}	1.07^{-1}	—	1.07^{-1}	—	—
f*	1.83	1.94	1.49	1.70	1.64	1.49	1.70

$$* f = \frac{\Sigma f_i}{n} \text{ with } f_i = \frac{S_{R\,calc}}{S_{R\,exp}} \text{ if } S_{R\,calc} > S_{R\,exp}$$

$$= \frac{S_{R\,exp}}{S_{R\,calc}} \text{ if } S_{R\,calc} < S_{R\,exp}$$

Table 5. Calculated and experimental sensitivity coefficients for copper samples (Fe: $S_R = 1$)

Element	Calculated S_R-value							Experimental S_R-value
	Addink	Kai, Miki	Goshgarian, Jensen	Honig	Ménétrier	Willardson, Socha	Vidal *et al.*	
Be	1	1.01	0.79	0.27	0.93	*	0.14	0.64 ± 0.09
Al	1.10	1.63	2.03	0.68	1.55	2.47	2.04	1.3 ± 0.2
Si	1.22	0.85	0.93	0.45	0.97	*	0.40	0.96 ± 0.09
P	8.22	5.09	3.96	3.34	5.28	*	1.06	1.6 ± 0.2
Cr	1	1.17	1.21	1.01	1.04	1.65	1.85	1.7 ± 0.2
Mn	1.75	1.50	1.57	1.53	1.49	1.21	1.92	1.5 ± 0.1
Co	1	0.94	0.90	0.87	0.89	*	0.88	0.88 ± 0.08
Ni	1	0.96	0.96	0.81	0.93	1.11	0.91	0.71 ± 0.07
Cu	1	1.20	1.18	0.78	1.16	1.06	0.84	0.68 ± 0.06
Zn	4.61	2.58	3.07	1.76	3.66	*	0.87	1.0 ± 0.1
Ga	1.16	1.83	1.93	0.89	1.42	2.45	2.63	1.9 ± 0.2
As	6.05	2.63	3.52	2.19	4.39	*	0.91	2.2 ± 0.6
Se	5.66	†	†	†	†	*	†	1.9 ± 0.4
Ag	1.39	1.46	1.84	1.74	1.77	1.1	2.03	1.8 ± 0.3
Cd	5.26	3.12	4.66	2.81	5.39	*	1.65	2.2 ± 0.5
Sn	1.31	1.40	2.14	1.21	2.00	1.26	1.52	2.3 ± 0.5
Sb	2.12	1.42	2.25	1.46	2.48	*	1.00	2.8 ± 0.7
Te	2.87	2.06	2.58	2.16	2.95	*	1.26	2.9 ± 0.5
Pt	1	0.64	0.74	§	0.85	*	§	0.8 ± 0.2
Pb	2.14	2.15	3.98	2.26	3.75	1.22	2.87	2.8 ± 0.7
Bi	2.53	2.08	4.20	§	3.89	1.29	§	1.7 ± 0.4
f‡	1.90	1.50	1.50	1.56	1.60	1.56	1.72	

* $\phi_x > \phi_z$

† ΔH unknown

§ Q unknown

‡ $f = \frac{\Sigma f_i}{n}$ with $f_i = \frac{S_{R\,calc}}{S_{R\,exp}}$ if $S_{R\,calc} > S_{R\,exp}$

$= \frac{S_{R\,exp}}{S_{R\,calc}}$ if $S_{R\,calc} < S_{R\,exp}$

Table 6. Calculated and experimental sensitivity coefficients for aluminium samples (Fe: $S_R = 1$)

Element	Calculated S_R-value						Experimental S_R-value
	Addink	Kai, Miki	Goshgarian, Jensen	Honig	Ménétrier	Vidal *et al.*	
Mg	3.55	2.80	4.38	1.54	4.25	1.74	3.0 ± 0.4
Al	1	1.63	2.03	0.68	1.55	2.04	1.08 ± 0.06
Si	1.11	0.85	0.93	0.45	0.97	0.40	0.84 ± 0.08
Ti	1	0.98	1.28	1.12	1.10	1.98	1.6 ± 0.2
Cr	1	1.17	1.21	1.01	1.04	1.85	1.6 ± 0.1
Mn	1.59	1.50	1.57	1.53	1.49	1.92	1.5 ± 0.1
Ni	1	0.96	0.96	0.81	0.93	0.91	0.74 ± 0.07
Cu	1	1.20	1.18	0.78	1.16	0.84	0.67 ± 0.05
Zn	4.21	2.58	3.07	1.76	3.66	0.87	1.8 ± 0.2
Sn	1.20	1.40	2.14	1.21	2.00	1.52	2.2 ± 0.3
Pb	1.95	2.15	3.98	2.26	3.75	2.87	2.8 ± 0.4
f*	1.48	1.36	1.39	1.43	1.41	1.49	

* $f = \frac{\Sigma f_i}{n}$ with $f_i = \frac{S_{R\,calc}}{S_{R\,exp}}$ if $S_{R\,calc} > S_{R\,exp}$

$= \frac{S_{R\,exp}}{S_{R\,calc}}$ if $S_{R\,calc} < S_{R\,exp}$

purity, the internal standard and the matrix, but also parameters connected with the sparking conditions and the temperature of the electrodes. These indeed have a large influence on the experimental sensitivity coefficients of elements with boiling and melting points considerably different from those of the internal standard, as shown earlier.[22]

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DETERMINATION OF TUNGSTEN BY PLASMA EMISSION SPECTROMETRY

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Summary—The emission spectrum of tungsten in an inductively coupled Ar/Ar-plasma (ICP) was investigated and relative intensities of 17 lines listed. Among the lines tested, W I 400.875 nm and W 207.911 nm are recommended for steel analysis. Several others suffer from severe spectral interferences. The line W 400.875 nm is very sensitive, but interfered with by titanium and very high iron concentrations. The line W 207.911 nm requires careful determination of adjacent background, but can be used even with low-resolution instruments. The influence of RF power, nebulizing conditions, burner height, and acid concentration was tested and found to be small enough for simple control in routine work. Steels and other alloys containing 0.02–80% W were analysed.

In 1963 Tappe and van Calker detected tungsten at the 25-ppm level in a non-toroidal plasma flame.[1] Since then, many elements have been tested with better equipment. Tungsten has been detected at concentrations of 0.4 ppm[2] and 0.1 ppm[3] but no investigation of the determination of tungsten with an inductively coupled plasma (ICP) has yet been published.[4]

EXPERIMENTAL

Apparatus

Sequential plasma emission spectrometer "Spectroanalyzer model JY 38 P", Instruments S.A. GmbH, D-8025 Unterhaching. RF generator 27.12 MHz, output power 1.6 kW. Torch for an inductively coupled Ar/Ar-plasma (12 l./min). Pneumatic nebulizer supplied by Instruments S.A., with Laval jet; inner tube of steel; jet cone of Teflon; body of Delrin; aspiration rate about 1 ml/min. Spectrometer: ISA-Jobin-Yvon HR 1000; 1-m Czerny-Turner mount, holographic grating 2400 lines/mm, linear dispersion 0.4 nm/mm; entrance slit 10 mm in height, 0.020 mm in width; exit slit 0.03 mm; photomultiplier Hamamatsu R 336. Computer and digital read-out: PDP 11. Chart recorder: Watanabe Servocorder SR 6201.

Chemical procedure

Approximately constant sample amounts of 0.1 g or, if necessary, 1 g are dissolved in a covered vessel in 10 ml of conc. phosphoric acid + 10 ml of conc. nitric acid + 20 ml of conc. hydrochloric acid + 20 ml of water. After dissolution is complete the liquid is diluted to 100 ml with water and this solution fed to the plasma flame. Smaller samples or further dilution are permissible for tungsten-rich material, provided the acid concentration is kept approximately the same. This dissolution procedure was successfully applied to ordinary, high-speed and heat-resistant steels as well as to Co/Ni/Cr alloys and hard-metal powders.

Recommended measurement conditions

RF power output: 0.9 kW (1.15 kW can also be used with rather good results); reflected power: 0.1 kW. Nebulizer: pressure 25 psig, argon flow-rate 0.45 l./min. Torch: argon flow-rate 12 l./min (working and cooling gas). Observation height: 0–10 mm above torch. Measurement: begin about 20–30 sec after starting the aspiration; integration time: 30 sec; sensitivity: "mesure" 18 or 21; background rate suppression: "zero" 0 (optionally higher, if desirable).

Calibration

Tungsten standard solution. Heat pure WO_3 at 800° to constant weight, dissolve it in sodium hydroxide solution and dilute with water.

Iron–tungsten standard solution. For steel analysis dissolve 0.100 g or 1.00 g of pure iron in the acid mixture used for samples, add an appropriate amount of tungsten standard solution and dilute to 100 ml with water. Prepare iron–tungsten standards covering the working ranges listed in Table 2.

For work with the line W 207.911 nm, the matrix concentrations of samples and standards must be closely matched. The analysis of iron alloys by use of the line W I 400.875 nm requires two different calibration curves for standardized iron concentrations of 0.1 g/ml and 1.0 g/ml, to allow for the spectral interference of iron. However, this interference is low enough for 0.1-g/ml iron standards to be usable for the evaluation of solutions with minor or no iron content; see Table 3.

RESULTS AND DISCUSSION

Selection of spectral line

Various tungsten lines have been used for conventional optical emission spectrometry.[4] Since the intensity values reported in the literature refer only to arc or spark excitation, an ICP emission spectrum of tungsten was recorded, over the range 402–200 nm. Conditions: 100 ppm W, aqueous solution; RF power: 1.15 kW; sensitivity: "mesure" 18; other instrument settings as recommended above. The relative intensities (W I 400.875 nm = 100) of several lines, and some additional data are given in Table 1.

Remarks on the line W I 400.875 nm

This line provides a high sensitivity in aqueous solution as well as in an iron–acid matrix. It suffers from spectral interference by the strong titanium line

Table 1. Spectral lines for tungsten analysis

Line, *nm*			Relative intensities: In ICP Ar/Ar 1.15 kW	Relative intensities: Harvey factor*, in graphite arc[5]	Relative intensities: In copper spark[6]	Remarks
Fe		407.47	0.03			matrix: Fe 10 mg/ml
W	I	407.436	45		550	
Ti	I	400.966	7	2		
Ti	I	400.893	38	1		
Fe		400.887	0.03			
W	**I**	**400.875**	100	0.02	950	high background in ICP
Mo	II	400.867	<0.05			
Ti	I	400.808	1	5		
W	I	381.748	15		160	
W	II	361.379	10			
Fe	I	321.594		1		
Nb	II	321.560		0.006		
W	I	321.556	56	0.05	130	OH band
W	I	294.698	64	0.015	300	R†; R.U.
Ta	I	294.691		1		
Mo		294.482		1		
V	II	294.457		0.05		
W	I	294.440	66	0.01	300	R; R.U.
Fe	II	294.439		0.5		
Cr	I	289.675		0.2		
W	I	289.645	46	0.05	190	
Re	I	289.602		0.4		
Fe	I	276.433		2		
Cr	I	276.435		1		
W	II	276.427	116	0.03		
Co	I	276.419		1		
Mn	II	272.445		5		
W	I	272.435	62	0.015	320	
Fe	I	271.902		1		
W	I	271.890	35		260	
Sb	I	271.889		0.3		
Cu	II	271.878		3		
Ge	I	258.919		0.3		
W	II	258.917	55			
Th		258.906		0.5		
W	I	255.135	44	0.03	280	lowest energy level involved
Fe		255.109		2		
Fe		243.634		5		
W	I	243.596	22	0.15	160	
Nb		243.596		1		
Co	II	239.739	high	0.2		
W	II	239.709	87	0.07		
Co	II	239.677		5		
W	II	220.449	11			
Fe		208.03	0.05			matrix: Fe 10 mg/ml
W		**207.911**	8			low background in ICP
Fe		207.81	0.02			matrix: Fe 10 mg/ml

* This factor is inversely proportional to intensity.
† R = self-reversal.

Ti I 400.893 nm and a weak iron line at 400.887 nm, which are both insufficiently separated by 1-m monochromators: see Figs. 1 and 2. A noticeable influence of iron on the intensity at the tungsten position 400.875 nm is observed for Fe:W ratios exceeding 50. For the determination of small amounts of tungsten in iron-rich material, samples and standards should not differ too much in iron content, see Table 3. The continuous background in this spectral region is generally high, but hardly influenced even by high iron concentrations. It may, if necessary, be measured at about 400.85 nm. Though the influence of large iron contents can readily be compensated, the high blank in the range of 400 nm prevents use of high sample concentration plus high gain. If extreme sensitivity is required, Fig. 4 (see below) suggests using low RF power to depress the background, at the risk of bad plasma stability and chemical interferences due to the lower temperature. Such conditions were not tested here. There is no spectral interference by at

Table 2. Statistical and calibration data

	W I 400.875 nm		W 207.911 nm		
Sensitivity "mesure"	21	18	21	21	21
Matrix	Fe 1 mg/ml	Fe 10 mg/ml	iron-free acid	Fe 1 mg/ml	Fe 10 mg/ml
Calibration factor, a (ppm W/digit/30 sec)	0.00269	0.0284	0.0359	0.0338	0.0381
Standard deviation of method, s (ppm W)	0.624	0.632	0.575	0.446	0.473
Degrees of freedom for s and s_a	13	13	5	8	8
Standard deviation of factor a, s_a (ppm W/digit/30 sec)	7.8×10^{-6}	1.6×10^{-4}	2.1×10^{-4}	1.3×10^{-4}	1.6×10^{-4}
Determination limit, c_d (ppm W)	0.13	1.4	1.7	1.6	1.8
Detection limit, x (net digits/30 sec)	34	34	34	34	34
Working range, (ppm W)	0.13–50* 0.13–20	1.4–500	1.7–700	1.6–600	1.8–700

* With background suppression.

least 100-fold amounts of Mo, V, Mn, Co, and Ni. For example, the line Mo II 400.867 nm, which is reported to have almost half the intensity of W I 400.875 nm in spark discharges,[7] was not observed at all in the Ar/Ar-ICP, proving its intensity to be less than 0.05% of that of the tungsten line.

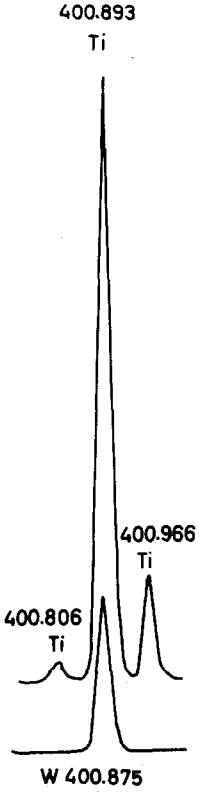

Fig. 1. Titanium lines near W I 400.875 nm (1000 ppm Ti in 6*M* HCl; 100 ppm W).

Remarks on the line W 207.911 nm

This line shows only 8% of the intensity of W I 400.875 nm, but the low background in its spectral region permits high gain to overcome this drawback. The background intensity near 208 nm is only about 0.8% of that near 400 nm (measured with 1.15 kW RF power). No interfering spectral lines of Fe and Ti in 1000-fold and of Mn, Cr, Co, Ni, V, and Mo in 100-fold amounts could be detected. The only neighbouring lines Fe 207.81 nm and Fe 208.03 nm are clearly separated from the tungsten line, even by instruments with moderate performance, see Fig. 3. On the other hand, the line W 207.911 nm suffers from pronounced matrix effects on both the net intensity of the line and the height of the continuous background. This demands, in any case, a careful control of the matrix content of samples and standards, even if the instrument provides a convenient measurement of the adjacent background. Consequently, the line W 207.911 nm is valuable for samples rich in titanium, and for monochromators with low resolution.

RF power

The RF power fed to the coil has relatively little influence on the net tungsten signal at 400.875 nm, but the background produced by water or an iron–acid matrix sharply increases with power, see Fig. 4.

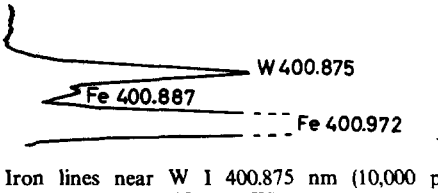

Fig. 2. Iron lines near W I 400.875 nm (10,000 ppm Fe + 10 ppm W).

Table 3. Examples of application

Sample	Tungsten, % Taken	Tungsten, % Found	Line, *nm*	Iron concn., *g/100 ml* In sample solution	Iron concn., *g/100 ml* In standard solution	Remarks
Steel	~0.02	0.03	400.875	~1	1	Interference by Fe 400.887 nm not fully compensated
		0.07	400.875	~1	0.1	
Steel	0.09	0.088	400.875	~0.1	0.1	
Steel	0.21	0.20	400.875	~0.1	0.1	
Heat-resistant Steel	2.21	2.27	400.875	~0.1	0.1	
		2.26	207.911	~0.1	0.1	
High-speed Steel	12.40	12.44*	400.875	~0.02	0.1	
		12.14*	207.911	~0.02	0.1	Improper correction of continuous background
Co/Cr Alloy	3.68	3.66	400.875	—	0.1	Fe-containing standards suffice
		3.74	207.911	—	0.1	Matrix effect on line and/or background
Hard-metal	80.0†	80.1*	400.875	—	0.1	Fe-containing standards suffice
		78.8*	207.911	—	—	

* Reduced amount of sample.
† Found by titration.

For the selection of measurement conditions it should be kept in mind, however, that low energy favours chemical interferences due to low kinetic plasma temperature.

Nebulizing conditions

Preliminary tests showed a nebulizing gas pressure of 25 psig and an aerosol argon flow-rate of 0.45 l./min to be favourable. Figure 5 demonstrates the influence of pressure and corresponding flow-rate on the tungsten and background signals. The initial values mentioned above were considered to be a good compromise and were kept constant in subsequent work, since high pressure produces larger aerosol particles and so favours interferences.

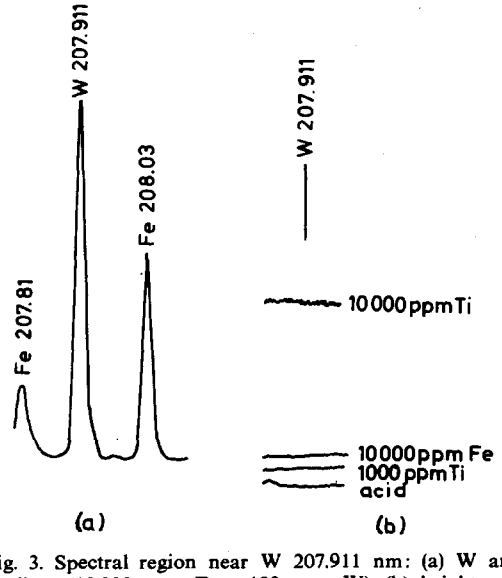

Fig. 3. Spectral region near W 207.911 nm: (a) W and Fe lines (10,000 ppm Fe + 100 ppm W), (b) height and structure of background near the tungsten line.

Since the level of the liquid being aspirated generally influences the signals, the importance of this parameter was tested for the ISA pneumatic nebulizer used. The effect was found to be noticeable but not

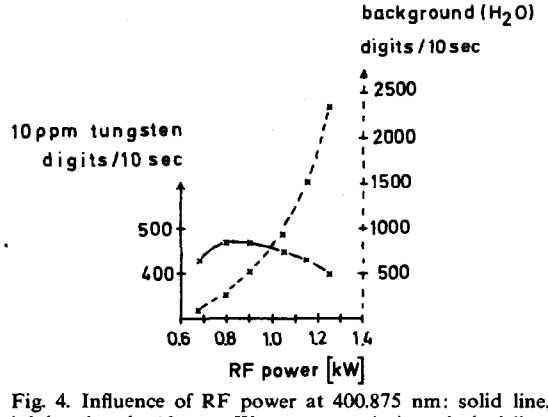

Fig. 4. Influence of RF power at 400.875 nm: solid line, left-hand scale, 10 ppm W, aqueous solution; dashed line, right-hand scale, background water.

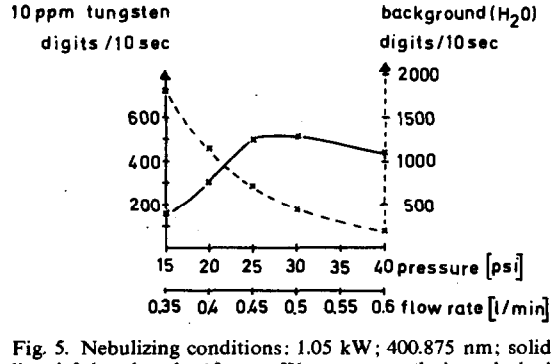

Fig. 5. Nebulizing conditions: 1.05 kW; 400.875 nm; solid line, left-hand scale, 10 ppm W, aqueous solution; dashed line, right-hand scale, background water. (The lower horizontal axis shows the flow-rates corresponding to the various pressures, if the argon rate is preset to 0.45 l./min at 25 psig.)

critical: deviations as large as ±50 mm from the level normally used caused variations of ±3% of the net tungsten signal.

Observation height

Normally the plasma flame region from 0 to 10 mm above the torch was observed. The tungsten 400.875 nm signal was the same in the region 4–14 mm above the torch but 20% less intense 10–20 mm above the torch.

Acid concentration

If the recommended chemical procedure is followed, the solution aspirated is 4.5*M* in phosphoric acid and about 3.8*M* in hydrochloric plus nitric acid. If the phosphoric acid concentration is kept constant, a decrease to 2.6*M* HCl + HNO_3 does not influence the tungsten signal, but a further reduction to 1.3*M* HCl + HNO_3 causes an error of +8%. At a constant acidity of 3.8*M* HCl + HNO_3 a decrease to 2.25*M* H_3PO_4 produces +6% error, and an increase to 6.8*M* H_3PO_4 gives an error of about −13%, due to the altered viscosity of the solution. Since the phosphoric acid content will hardly vary at all in routine work, and since even considerable losses of the other two acids are harmless, the acid concentration is not a parameter requiring careful control. This is mainly due to the excellent properties of the ISA nebulizer used.

Calibration and statistical characterisation

Calibration measurements were performed at 400.875 and 207.911 nm, by the recommended experimental procedures. The standard solutions contained tungsten at the prescribed acid concentration (4.5*M* H_3PO_4 + 2.4*M* HCl + 1.4*M* HNO_3) with or without a matrix of 1 or 10 mg of iron per ml. The background was separately determined by aspirating tungsten-free samples.

The gross readings x_g (digits/30 sec) are corrected for the blank x_{bl}, and the resulting net values x_n (digits/30 sec) are converted into concentrations c (ppm W in the solution aspirated). The equation used is $c = ax_n$, with the calibration factor a (ppm/digit/30 sec) listed in Table 2.

Correlation analysis proved the strict linearity of all calibration curves (significance level $P = 99.9\%$). Regression analysis of the expression $y = ax + b$ showed $b = 0$ (at the 95% level and with the degrees of freedom listed in Table 2), *i.e.*, the applied method of background correction is efficient. The determination limit ("Erfassungsgrenze") c_d (ppm W) is calculated according to the definition of Svoboda and Gerbatsch[8] ($x_d = \bar{x}_{bl} + 6\sigma_{bl}$) to give $c_d = 6a\sigma_{bl}$ for net values x_n. The detection limit ("Nachweisgrenze") $\underline{x}$ (net digits/30 sec) is given according to Kaiser and Specker[9] as $\underline{x} = \bar{x}_{bl} + 3\sqrt{2}\sigma_{bl}$, calculated for net digits.

Applications

Table 3 shows the results obtained for steels and non-ferrous alloys. They prove that the line W 400.875 nm suffers little from matrix effects, except for very high iron concentrations. When the line W 207.911 nm is used, however, matrices of samples and standards must be carefully matched.

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UNUSUAL COMPLEXING PROPERTIES OF 2-(2′-PYRIDYL)- AND 2-HYDRAZINO-8-HYDROXYQUINOLINE

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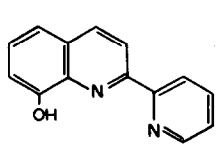
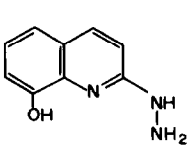
Summary—The ligands 2-(2′-pyridyl)- and 2-hydrazino-8-hydroxyquinoline form terdentate complexes with a 5,5-bicyclic ring system, the stabilities being greater than those of the corresponding 8-hydroxyquinolinates. This study affords a more complete picture of the behaviour of terdentate 2-substituted 8-hydroxyquinolines. Solutions of these ligands and metal ions are complicated by formation of the protonated species MHL^{2+}, $M(HL)_2^{2+}$ and $MLHL^+$. The existence of the protonated species is dependent not only on pH and ligand:metal-ion molar ratio but also on the nature of the metal ion itself.

In studies on the design of selective analytical reagents, 2-substituted 8-hydroxyquinolines have received considerable attention. Although early work with these ligands focused on the effects of 2-alkyl and 2-aryl substituents,[1–3] more recent work has investigated the effects of 2-substituents that contain a potential donor atom.[4–7] Evidence presented in a previous report[7] suggested that the most stable terdentate complexes derived from such substituted 8-hydroxyquinolines result when the relative orientation of the three donor atoms is such that a 5,6-bicyclic chelate-ring system is produced. This ring system is strain-free, as shown by molecular models. For a donor-atom orientation that imposes a 5,5-bicyclic ring system, a higher degree of chelate-ring strain is encountered. If the degree of strain is minor (as in the complexes of 2-aminomethyl-8-hydroxyquinoline), terdentate complexes of greater stability than the corresponding 8-hydroxyquinoline complexes are formed.[7] If the strain is appreciable, the resulting complexes may be terdentate but of little enhanced stability (*e.g.*, complexes of 4-amino-5-hydroxyacridine),[4] or bidentate in which the 2-substituent acts as a blocking group (*e.g.*, complexes of 4,5-dihydroxyacridine and of 8-hydroxyquinoline-2-carboxaldoxine).[4,6]

The present study reports on the complexing properties of 2-(2′-pyridyl)- and 2-hydrazino-8-hydroxyquinoline (2-PyQ and 2-HyQ, respectively). Each ligand can form a 5,5-bicyclic chelate-ring system.



2—PyQ



2—HyQ

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Solutions of these ligands and metal ions are very complicated, containing several different metal–ligand species, some of which are unusual. An attempt to describe these solutions quantitatively has been made. Formation constants for the various species have been calculated and data for the 1:1 ML^+ species show clearly that these ligands form terdentate complexes of enhanced stability.

EXPERIMENTAL

Reagents

All chemicals used were of suitable purity for the purpose intended. Purification of 1,4-dioxan and the preparation and standardization of stock metal-ion solutions were as described elsewhere.[7]

The ligand 2-PyQ was synthesized from 8-methoxyquinoline and 2-pyridyl-lithium by a procedure similar to that used for 2-(2′-hydroxyphenyl-8-hydroxyquinoline.[7] The 2-pyridyl-lithium was prepared by the procedure of Gilman and Spatz,[8] except that the temperature was maintained at −40° for an improved yield.[9] The crude 2-PyQ was recrystallized from aqueous ethanol, m.p. 129–130°; yield, 20% based on 8-methoxyquinoline. Calculated for $C_{14}H_{10}N_2O$: C, 75.6%; H, 4.54%; N, 12.6%; found: C, 75.5%; H, 4.4%; N, 12.5%. The ligand 2-HyQ was prepared as described by Rudolph *et al.*,[10] m.p. 177–178°. Calculated for $C_9H_9N_3O$: C, 61.7%; H, 5.18%; N, 24.0%; found: C, 61.8%, H, 5.5%, N, 24.0%. These ligands were further characterized by infrared, 100-MHz proton magnetic resonance (^{1}Hmr), and mass spectroscopy. All spectra were consistent with the expected functional groups and structures. The more notable features were the absence of the α-H resonance (a quartet in 8-hydroxyquinoline) in the second-order ^{1}Hmr spectra, proving that substitution had occurred in the 2-position, and the correct parent molecular-ion peaks in the mass spectra. Both ligands absorb strongly in the ultraviolet region. For 2-PyQ, $\epsilon_{H_2L^+} = 3.2 \times 10^4$ l.mole^{-1}.cm^{-1} at $\lambda_{max} = 296$ nm (pH 2); $\epsilon_{HL} = 3.0 \times 10^4$ and 3.1×10^4 at $\lambda_{max} = 280$ and 263 nm, respectively (pH 7); $\epsilon_L = 3.3 \times 10^4$ at $\lambda_{max} = 295$ nm (pH 13). For 2-HyQ, $\epsilon_{H_2L^+} = 4.2 \times 10^4$ at $\lambda_{max} = 266$ nm (pH 3); $\epsilon_{HL} = 4.7 \times 10^4$ at $\lambda_{max} = 278$ nm (pH 9); $\epsilon_L = 4.4 \times 10^4$ at $\lambda_{max} = 262$ nm (pH 12).

Acid-dissociation constants

The pK(NH) and pK(OH) values were obtained potentiometrically, essentially as described elsewhere.[7,11] Appropriate volume corrections and glass-electrode calibration for hydrogen-ion concentrations were made for the 50% v/v aqueous dioxan medium (ionic strength, 0.1). The pK_w value was 15.33 ± 0.02 at 25°. The pK values were calculated from straightforward equations. Only experimental points which fell in the ranges $\bar{p}$ = 0.2–0.8 and 1.2–1.8 were used. For 2-PyQ, pK(NH) = 3.62, pK(OH) = 11.21; for 2-HyQ, pK(NH) = 6.58, pK(OH) = 11.86. These values are the average of 10–12 results, with standard deviations ≤0.03.

Metal-chelate formation constants

These were determined potentiometrically in the usual way in 50% v/v dioxan–water.[4,11] The hydrolysis curve for each metal ion was also obtained. The program SCOGS, which allows calculation of formation constants and the determination of the types of metal-complex species present, was used in this work.[12] With SCOGS, it is possible to calculate formation constants not only for simple complexes but also for protonated, hydrolysed, mixed and polynuclear complexes in a system in which the degree of complexation is pH-dependent. Where reliable constants are to be calculated for many co-existing species, it is essential to have experimental data of high accuracy covering a wide range of experimental concentrations of ligands and metal ion. Thus, the data from as many as 8 (and not fewer than 3) different ligand:metal-ion molar ratios (ranging from 9:1 to 1:1) were refined together. The use of SCOGS entailed a correction in the term CT1TR[13] and revision to suit the 2-Py-Q and 2-HyQ systems. Whenever appropriate, the interpretation of the more complicated titration curves was assisted by the use of formation curves, species distribution diagrams and polarographic and ultraviolet–visible region spectral studies.

RESULTS AND DISCUSSION

From absorption spectra of 2-PyQ solutions in the range from 3M hydrochloric acid to pH 13, only the acid–base forms H_2L^+, HL and L^- were indicated. The species H_3L^{2+} was not detected, even in the 3M acid. This result is consistent with the protonation behaviour of 2,2′-bipyridyl and 1,10-phenanthroline for which Beattie and Webster[14] showed that H_2L^{2+} is formed only in concentrated acid solutions. For 2-HyQ, H_3L^{2+} was detected in the acidity range from 3M hydrochloric acid to pH 1.5 but the pK_a value was not determined. The pK(NH) value (6.58) was assigned to the hydrazino group, since for hydrazine the pK_a value is 7.98 (in water, at 25.0°).[15] The higher value for pK(OH) (11.86) relative to that for 8-hydroxyquinoline (11.20)[6] is the result of hydrogen-bonding between the –OH and hydrazino groups, as revealed by ^{1}Hmr and infrared spectra.

The complexing properties of 2-PyQ and 2-HyQ are both complicated and unusual. Each ligand forms non-protonated and protonated complexes, the relative amounts of which depend not only on pH and the ligand:metal-ion molar ratio but also on the nature of the metal ion. Thus, with Mn(II), only the species ML^+ and ML_2 are formed. The titration and formation curves for Mn(II) with both ligands were typical of those obtained for bivalent ions and 8-hydroxyquinoline and there was no indication of protonated complexes from these curves or from the SCOGS refinement of the potentiometric data. With Co(II), Ni(II), Zn(II) and Cd(II), however, the formation of protonated species was evident and for an adequate description of the systems by SCOGS refinement, the following species were required: ML^+, ML_2, MHL^+, $M(HL)_2^{2+}$ and $MLHL^+$. The Ni(II)/2-PyQ system is typical and is presented here. The behaviour of Cu(II) was different and is discussed later.

In the titration curves for the Ni(II)/2-PyQ system at ligand:metal-ion ratios of 9:1, 5:1 and 2:1, two buffer zones were observed, each corresponding to one mole of base per mole of Ni(II). The second zone (pH 5.5–7) was not altered by changes in the 2-PyQ concentration and could not be attributed to hydrolysis, which occurred in the pH range 8–9 in the titration with a 1:1 ratio. For this ratio, the two buffer zones corresponded to 0.5 mole of base per mole of Ni(II) and the pH range of the second zone (5.5–7) was unchanged. Consistent with these observations is the scheme:

$$Ni^{2+} + 2HL \rightleftharpoons NiLHL^+ + H^+ \quad \text{(pH 3–5)}$$

$$NiLHL^+ \rightleftharpoons NiL_2 + H^+ \quad \text{(pH 5.5–7)}$$

where the formation of $NiLHL^+$ is thought to occur by the addition of HL to NiL^+.

Additional indirect evidence for protonated species was deduced from the formation curves (Fig. 1). The maximum displayed in these curves is unusual and gives rise to the same value of $\bar{n}$ at three different pL values. The peculiar shape is indicative of incorrect chemical equations used to describe the system. These equations were based on the assumptions that the only complexes formed are NiL^+ and NiL_2 and that any protons bonded to donor atoms are liberated on chelation. The formation curves are still useful, however, if interpreted in terms of the number and source of protons liberated instead of the average number of ligands bound per Ni(II) at a given pL value. In acidic solution, $\bar{n}$ = 1 corresponds to two protons liberated per Ni(II) (from the NH and OH

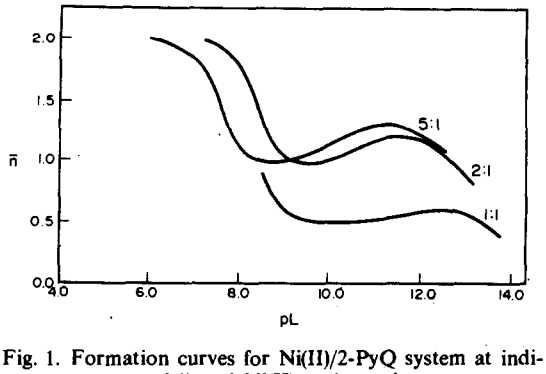

Fig. 1. Formation curves for Ni(II)/2-PyQ system at indicated ligand:Ni(II) molar ratios.

groups), but above pH 4–5 it corresponds to the liberation of only one proton, which must come from the OH group. In Fig. 1, starting at low pH values (high pL values), $\bar{n}$ increases to a maximum above 1 and then decreases to unity at pL ~ 9.5 and 8.5 (~pH 4.0 and 5.0 for 5:1 and 2:1 ratios, respectively). Since below pH 4.0 and 5.0, $\bar{n} > 1$, it is necessary to postulate the formation of a species such as $NiLHL^+$ where the proton liberated from H_2L^+ is from the NH group. If $NiLHL^+$ is the most stable species formed in acidic solution (for molar ratios $\geq 2:1$), $\bar{n}$ should attain a maximum value of 1.5 since the overall reaction involves the release of three protons. For a 5:1 ratio, $\bar{n}_{max} = 1.35$ and for a 9:1 ratio, $n_{max} = 1.50$.

At pH above 4–5, $NiLHL^+$ is in equilibrium with free 2-PyQ as follows:

$$NiLHL^+ \rightleftharpoons NiL^+ + HL$$

Since this reaction does not involve the release of protons, the formation of $NiLHL^+$ cannot be detected with a glass electrode as probe. Thus, $\bar{n}$ should decrease to unity from its maximum value, as is observed when the pH is raised to ~4.0–5.0 (Fig. 1). As noted earlier, the pH range (5.5–7) for the acid dissociation of $NiLHL^+$ is not dependent on the free ligand concentration, provided the formation of $NiLHL^+$ is essentially complete prior to acid dissociation. The species distribution diagram (Fig. 2) shows that $NiLHL^+$ is essentially fully formed at ~pH 4.5 and that its concentration decreases as that of NiL_2 increases from ~pH 5–7. Thus, the species distribution diagram, based on equilibrium constants obtained by SCOGS refinement, is entirely consistent with the interpretations of the basic titration curve and of the formation curves based on "proton release". Such consistency was also obtained for the Co(II), Zn(II) and Cd(II) systems of 2-PyQ and 2-HyQ.

The formation curve for the Ni(II)/2-PyQ system at a 1:1 ratio is also representative and is of special interest in that $\bar{n}$ values of 0.5 rather than 1.0 were obtained over a wide pL range (Fig. 1). At pL = 9.5, $\bar{n} = 0.5$, showing that half of the available quinoline OH protons were liberated. In more acidic solution (*e.g.*, pL = 12.5), $\bar{n}$ increases above 0.5, which is indicative of the formation of protonated species. Nearly half of the total Ni(II) is uncomplexed, as confirmed by polarographic and spectral analysis. To explain this observation, it is necessary to postulate that the equilibrium constant for the attachment of HL to NiL^+ is greater than that for the formation of NiL^+, the concentration of which must necessarily be small. The enhanced stability of the $MLHL^+$ species is general (Table 2) and is discussed further below. Persuasive evidence that the Ni(II)/2-PyQ system has been correctly characterized is presented by the species distribution diagram (not shown) for a 1:1 molar ratio. At ~pH 4.5, $\alpha_{Ni(II)free}$ is ~0.5, α_{NiHL^+} ~0.4 and α_{NiL^+} and $\alpha_{NiHL_2^+}$ are ~0.05. At pH 6.5, (all ligand now complexed), $\alpha_{Ni(II)free}$ is ~0.4, α_{NiLHL^+} has decreased to ~0.2 (because of deprotonation to NiL_2), α_{NiL_2} has increased from 0 to 0.2 and, most importantly, α_{NiL^+} has *increased* to ~0.2. The increase in α_{NiL^+} is not contradictory but is indeed expected because, unlike $NiLHL^+$, NiL_2 is not stabilized.

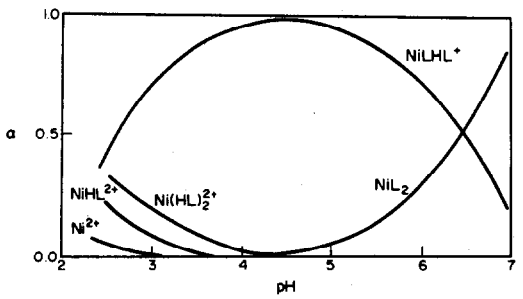

Fig. 2. Species-distribution diagram for Ni(II)/2-PyQ system at 2:1 ligand:Ni(II) molar ratio.

Formation constants are given in Table 1. Not obvious from Table 1 is the special stability of the $MLHL^+$ complexes. The enhanced stability for the addition of HL to ML^+ in relation to the addition of HL to M(II) can be demonstrated by comparing the difference between the stepwise constants $K^{ML}_{MLHL} = [MLHL^+]/[ML^+][HL]$ and $K_{MHL} = [MHL^{2+}]/[M^{2+}][HL]$. This difference is expressed by

$$\Delta \log K = \log K^{ML}_{MLHL} - \log K_{MHL}$$
$$= \log \beta_{MHL_2} - \log \beta_{ML} - \log \beta_{MHL} \quad (1)$$

(This equation also provides the (log) difference between the constants $K^{MHL}_{MLHL} = [MLHL^+]/[MHL^{2+}][L^-]$ and $K_{ML} = [ML]/[M^{2+}][L^-]$.)

In the absence of special stabilizing factors, values of $\Delta \log K$ (Table 2) should be <0. It is logical to

Table 1. Log of formation constants* of 2-PyQ and 2-HyQ with selected metal ions, in 50% v/v aqueous dioxan, ionic strength = 0.1, at 25°

	β_{ML}	β_{ML_2}	β_{MHL}	$\beta_{MH_2L_2}$	β_{MHL_2}
			2-PyQ complexes		
Mn(II)	8.44	16.50	—	—	—
Co(II)	11.07	22.42	15.50	29.8	28.1
Ni(II)	11.8	24.0	16.6	32.8	30.4
Cu(II)	14.65	22.75	—	—	—
Zn(II)	10.89	21.61	14.64	29.85	27.5
Cd(II)	9.1	19.6	14.7	29.1	25.6
			2-HyQ complexes		
Mn(II)	8.81	16.46	—	—	—
Co(II)	10.6	21.9	16.2	32.8	28.6
Ni(II)	11.3	22.7	16.9	34.8	30.5
Cu(II)	16.04	25.87	18.90	38.20	34.0
Zn(II)	10.3	21.8	16.8	34.6	29.4
Cd(II)	8.6	19.3	16.7	33.2	27.2

* All constants are expressed as $\beta_{MH_iL_j} = [MH_iL_j]/[M][H]^i[L]^j$.

Each value represents the data from at least three titrations, refined together.

The standard deviations (not shown) ranged from 0.03 to 0.4, the poorer precision being obtained for the Zn(II) and Cd(II) complexes.

Table 2. Stabilization (Δ log K values) of $MLHL^+$ complexes of 2-PyQ and 2-HyQ

	$\log K^{ML}_{MLHL}$	$\log K_{MHL}$	$\Delta \log K$
	2-PyQ complexes		
Co(II)	5.8	4.3	1.5
Ni(II)	7.4	5.4	2.0
Zn(II)	5.4	3.4	2.0
Cd(II)	5.3	3.5	1.8
	2-HyQ complexes		
Co(II)	6.1	4.3	1.8
Ni(II)	7.3	5.0	2.3
Cu(II)	6.1	7.0	−0.9
Zn(II)	7.2	5.1	2.1
Cd(II)	6.7	5.8	0.9

assume that the enhanced stability is due to the proton in $MLHL^+$. From the following considerations, it was concluded that the proton is associated with an oxygen rather than a nitrogen atom: (*a*) since the proton in the $MLHL^+$ chelates dissociates at pH >5 for the 2-PyQ chelates (and at pH >6.5 for the 2-HyQ chelates), it is most unlikely that it is bonded to a nitrogen atom because the effect of the co-ordinated metal ion would be to reduce the pK(NH) value;[16] (*b*) no protonated complexes, including $MLHL^+$, were found with Mn(II). This is consistent with the fact that Mn(II) forms appreciably more stable complexes with oxygen than with nitrogen ligands.[17] Thus, the preference of the metal ion for oxygen or nitrogen donors could determine the formation of protonated species.

The enhanced stability associated with the addition of HL to ML^+ must be the result of the hydrogen-bonding. In this respect, the $MLHL^+$ complexes resemble the bis(dimethylglyoximato)nickel(II) complex for which solution studies have shown that $K^{MHL}_{M(HL)_2} > K_{MHL}$.[18] The stabilization of $MLHL^+$ is ~2 log units (Table 2), which represents ~3 kcal/mole, an amount of energy readily provided by hydrogen-bonding. However, unambiguous evidence of hydrogen-bonding in the solid $NiLHLClO_4$ (HL = 2-PyQ) was not seen in the infrared spectrum. The O-H---O frequency appears to be shifted to frequencies lower than expected as in the Ni(II)–dimethylglyoxime chelate.[19] Nevertheless, molecular models suggest that for octahedral co-ordination both oxygen donors must be in adjacent co-ordination sites and that the distance between these donors is appropriate for hydrogen-bonding.

In summary, the following complexation reactions of 2-PyQ and 2-HyQ with Co(II), Ni(II), Zn(II) and Cd(II) are proposed (pH ranges are shown to the right):

	2-PyQ	2-HyQ
$M^{2+} + H_2L^+ \rightleftharpoons MHL^{2+} + H^+$	2.5–3.5	4–6
$MHL^{2+} + H_2L^+ \rightleftharpoons M(HL)_2^{2+} + H^+$	2.5–3.5	4–6
$M^{+2} + H_2L^+ \rightleftharpoons ML^+ + 2H^+$ (small amounts)	2.5–3.5	4–5
$ML^+ + H_2L^+ \rightleftharpoons MLHL^+ + H^+$	2.5–5.0	4–7
$MLHL^+ \rightleftharpoons ML_2 + H^+$	5.0–7.0	6–8

The reactions with Cu(II) and 2-PyQ are different in three respects. The species $CuHL^{2+}$ and $Cu(HL)_2^{2+}$ are not formed in noticeable amounts; at a 1:1 ratio of metal to ligand, CuL^+ predominates over $CuLHL^+$, with little free Cu(II) remaining; and the difference between β_{CuL_2} and β_{CuL} is strikingly small. This is attributed to tetragonal distortion, prevalent among 6-co-ordinated Cu(II) complexes, in which the four planar bonds are strengthened and the axial bonds weakened (Jahn–Teller effect).[20] If the first ligand forms three bonds *in the plane* compared to only one for the second ligand, CuL^+ would be stabilized relative to CuL_2. The stabilization would also account for the preferred formation of CuL^+ instead of $CuLHL^+$ at a 1:1 molar ratio and for the negligible concentration of $CuHL^{2+}$ and $Cu(HL)_2^{2+}$. The fact that observable amounts of these protonated species are formed by 2-HyQ could result from the greater basicity of the nitrogen donors, which would stabilize the protonated bidentate complexes.

The values of β_{ML} (Table 1) show that the non-protonated 1:1 complexes of both 2-PyQ and 2-HyQ are more stable than the corresponding complexes of 8-hydroxyquinoline (see Table 1 in reference 7). This is strong evidence that the ligands are terdentate in these complexes. The increase in stability, however, is not large and supports the suggestion from molecular models that the bite of these ligands is loose and that some strain exists in closing the 5,5-bicyclic ring structure, particularly for the 2-HyQ chelates. In view of the increased total basicity of the donor atoms of 2-HyQ over that for 8-hydroxyquinoline, the stability of the increase in total basicity of the donor atoms of enhanced. In this regard, both ligands are similar to 2-aminomethyl-8-hydroxyquinoline.[6,7] The results of this work confirm the opinion[7] that the most stable complexes derived from potentially terdentate 2-substituted 8-hydroxyquinolines will result when a 5,6-bicyclic ring system can be formed, as is the case with 2-(2′-hydroxyphenyl)-8-hydroxyquinoline.[7] Such ligands would form very stable complexes, rivalling the stability of EDTA complexes. Also, not being especially selective, these ligands would react simultaneously with several metal ions under a single set of conditions and could be very valuable as preconcentration extractants for groups of metal ions (*e.g.*, in sea-water) in ultratrace analysis.

Acknowledgement—We wish to thank the National Research Council of Canada for the financial support of this study.

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COMPLEX-FORMING PROPERTIES OF SUBSTITUTED *N*-HYDROXYACETOACETANILIDES WITH BIVALENT AND TERVALENT METAL IONS

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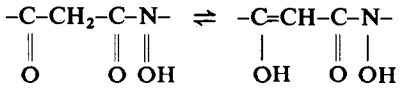
Summary—From spectroscopic studies as well as from the stability constants of their complexes with metal ions, it has been observed that substituted *N*-hydroxyacetoacetanilides do not enolize, because of strong hydrogen bonding in the hydroxamic moiety $CH_3.CO.CH_2.CO.N(OH).R$ hindering the movement of the $CH_3.CO.CH_2-$ group. The ligands thus behave as bidentate in contrast to the expected terdentate nature. The stability constants of their complexes are comparable with those for complexes of other ligands in which oxygen is the donor.

Extensive studies have been made on the analytical applications of hydroxamic acids for the determination of several bivalent and tervalent metal ions.

There is renewed interest in these chelating agents because of their widespread importance in certain iron-transport substances and further they have been found in natural products such as antibiotics and bacterial growth factors. In all of them the hydroxamic acid group –CO–N(OH)– acts as a typical bidentate donor and the chelating reactions with metal ions are very similar to those of acetylacetone.

Physicochemical investigations on the co-ordination behaviour of chelating agents, namely *N*-hydroxyacetoacetanilide and its substituted derivatives comprising both the hydroxamic acid and the β-diketone moieties, have not been made. Such reagents have the possibility of enolizing



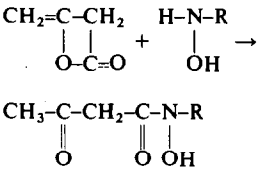
and thus could act as the terdentate ligands. The present communication concerns preparation of these ligands and their characterization by spectroscopic studies. In addition the stability constants of the complexes formed by them with Cu, Ni, Mn, La, Pr, Nd, Sm, Gd, Tb, Y and Yb have been determined by potentiometric titration in 70% v/v dioxan/water solvent mixture at 20°.

EXPERIMENTAL

Reagents

Preparation of the complexing agents. *N*-Arylhydroxylamines and 2-(hydroxyamino)benzo[*d*]-1,3-thiazole were prepared according to published methods. Some of the ligands mentioned here have been described previously.[1]

The ligands were prepared by condensing the substituted hydroxylamines with diketene in dry ether at 0°.



The hydroxylamines (0.1 mole) were dissolved in about 60 ml of dry ether and cooled to 0°. Freshly distilled diketene (0.1 mole) in 20 ml of dry ether was then added over a period of an hour. The white compounds precipitated were filtered off, washed with cold ether and recrystallized from benzene.

Because of the insolubility of 2-(hydroxyaminobenzo-[*d*]-1,3-thiazole in ether, the condensation was done in methanol.

Preparation of the metal complexes. The copper complexes were made by the method of Kettrup *et al.*[2–4] To a hot solution of the ligand (0.01 mole) in 10 ml of dioxan/water (1:1) was added dropwise copper octoate (5×10^{-3} mole) dissolved in 20 ml of ether. After the addition, the mixture was refluxed for 45 min and the precipitated complex was purified by washing with petroleum ether and finally with diethyl ether.

The complexes of nickel, lanthanum and yttrium were prepared by adding an ethanolic solution of the ligands to the aqueous solution of the metal salts, heated to 50–60°. The complexes could be precipitated by dropwise addition of dilute sodium hydroxide solution.

Apparatus

Infrared spectra were recorded in KBr pellets with a Perkin-Elmer 225 spectrophotometer. NMR measurements were done on $CDCl_3$ solutions with a Varian EM-390 90 MHZ spectrometer at room temperature with TMS as internal standard. Mass spectra were taken on an SM 1 double-focusing mass spectrometer (Varian MAT).

Potentiometric titrations

A Metrohm Super Potentiograph, type E 436, with an E 121 UX electrode (Metrohm, pH 0–14, 15–100°) was used. For the determination of stability constants, 2.5 ml of 5*M* sodium perchlorate, 5 ml of 0.1*M* metal perchlorate or nitrate, 30 ml of dioxan and 5 ml of 0.4*M* ligand solution in dioxan were placed in a 100-ml beaker and stirred for 20 min. The solution was then titrated with carbonate-free 1*M* sodium hydroxide added at a rate of 1 ml/min. All

Table 1. Elemental analyses, melting points and mass spectra of $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-N(OH)-R$

No.	Ligand	R	M.p. °C	C, %*	H, %*	N, %*	Molecular peak, *m/e*	*I*, %(M^+.)
I	*N*-Hydroxyacetoacetanilide	C_6H_5	124°	62.2 (62.00)	5.7 (5.64)	7.2 (7.54)	193	18
II	4-Methyl-*N*-hydroxyacetoacetanilide	p-CH_3-C_6H_4	125°	63.8 (63.94)	6.3 (6.10)	6.8 (6.86)	207	16
III	3-Methyl-*N*-hydroxyacetoacetanilide	m-CH_3-C_6H_4	105°	63.8 (63.73)	6.3 (6.21)	6.8 (6.85)	207	15
IV	4-Fluoro-*N*-hydroxyacetoacetanilide	p-F-C_6H_4	115°	56.9 (56.85)	4.8 (4.87)	6.6 (6.59)	211	18.5
V	4-Chloro-*N*-hydroxyacetoacetanilide	p-Cl-C_6H_4	138°	52.8 (52.94)	4.4 (4.45)	6.2 (6.13)	227	11
VI	4-Bromo-*N*-hydroxyacetoacetanilide	p-Br-C_6H_4	137°	44.1 (44.25)	3.7 (3.80)	5.1 (5.17)	272	13
VII	4-Iodo-*N*-hydroxyacetoacetanilide	p-I-C_6H_4	127°	37.0 (36.85)	3.2 (3.27)	4.4 (4.57)	319	14
VIII	2-(*N*-Acetoacetyl-*N*-hydroxyamino)benzo[*d*]-1,3-thiazole	C_7H_3NS	—	52.8 (52.95)	4.0 (4.23)	11.2 (11.22)	250	11

* Figures in parentheses are the theoretical values.

Table 2. ^{1}H-NMR data for the ligands in $CDCl_3$ solvent, *ppm*

Ligand*	$CH_{3\,(al)}$	$CH_{3\,(ar)}$	CH_2 A	CH_2 B	J_{AB}	Ring protons	OH
I	1.61	—	2.68	3.12	15.6	7.00–7.73	5.95
II	1.61	2.27	2.68	3.09	15.6	7.08–7.73	5.95
III	1.61	2.32	2.68	3.12	15.9	6.88–7.48	5.90
IV	1.61	—	2.69	3.14	16.5	7.04–7.78	5.93
V	1.61	—	2.68	3.12	17.7	7.30–7.73	5.96
VI	1.62	—	2.68	3.11	15.6	7.40–7.77	5.95
VII	1.62	—	2.50	3.04	15.6	7.44–7.70	5.94
VIII	1.70	—	2.25	2.60	15.0	7.00–8.05	5.95

* Serial numbers refer to Table 1.

titrations were done at 20 ± 0.50°. For the determination of acid dissociation constants, the same method was used but the metal solutions were omitted. The stability constants were calculated by Bjerrum's method as modified by Calvin and Wilson.[5] The acid dissociation constants were determined by using Henderson's equation according to Meites and Goldman.[6]

RESULTS AND DISCUSSION

The results of elementary analysis, melting points and molecular peak *m/e* values (from mass spectra) of the ligands are summarized in Table 1. The mass spectrum of *N*-hydroxyacetoacetanilide shows a base peak with high intensity, at *m/e* 109 (taken as reference), corresponding to the fragmentation ion $C_6H_6ON^+$. Similar base peaks with high intensities were also observed for the other substituted ligands. The fragmentation patterns are simple and all very similar.

The mass spectroscopic studies of the copper complexes show no molecular peak and no metal-containing fragmentation ion, which may possibly be due to their low stability constants log (K_{av} < 8). This corroborates the observation of Kettrup and Riepe,[7] from their mass spectral studies on acetoacetanilides, that metal complexes with stability constants log K_{av} < 8.5 do not give any molecular peak. From NMR spectra of the ligands, as described in Table 2, it is observed that no enolization similar to that of acetylacetone takes place in solution, as no additional signal could be found for the second hydroxyl proton in

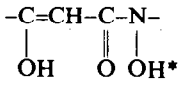


Table 3. Elemental analyses, melting points and infrared spectra of copper complexes

Ligand	C, %*	H, %*	N,%*	Frequency, cm^{-1} $\nu_{C=O-H}$	$\nu_{C=O\rightarrow M}$
I	53.6 (54.25)	4.5 (4.63)	6.7 (6.12)	1670 S	1570 S
II	55.5 (55.50)	5.11 (5.14)	5.9 (6.06)	1665 S	1565 S
III	55.5 (54.70)	5.11 (5.42)	5.9 (6.03)	1670 S	1585 S
IV	51.4 (49.89)	4.3 (4.24)	6.0 (6.07)	1670 S	1570 S
V	49.7 (49.16)	4.2 (4.62)	5.8 (6.09)	1670 S	1565 S
VI	45.5 (44.84)	3.8 (3.71)	5.3 (5.12)	1670 S	1550 S
VII	—	—	—	1650 m	—
VIII	—	—	—	1685 S	—

* Figures in parentheses are the theoretical values.

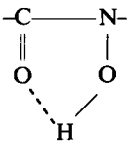
Table 4. Stability constants of Cu, Ni and Mn complexes of substituted *N*-hydroxyacetoacetanilides

Substituent	pK	CuL_2 log K_1	log K_2	log K_{av}	NiL_2 log K_1	log K_2	log K_{av}	MnL_2 log K_1	log K_2	log K_{av}
—	10.93	9.24	6.9	8.0	6.0	4.54	5.22	6.19	3.62	4.73
4-Methyl	11.00	9.35	7.25	8.23	5.9	4.65	5.24	5.19	3.65	4.35
4-Fluoro	10.81	7.55	—	—	—	—	—	—	—	—
4-Chloro	10.89	8.55	6.5	7.45	5.75	4.5	5.09	4.96	4.48	4.71
4-Bromo	10.90	7.96	6.52	7.16	5.67	4.03	4.78	5.57	3.22	4.24

Table 5. Stability constants of lanthanide complexes of substituted *N*-hydroxyacetoacetanilides

Substituent	LaL_3				PrL_3				NdL_3				SmL_3			
	log K_1	log K_2	log K_3	log β	log K_1	log K_2	log K_3	log β	log K_1	log K_2	log K_3	log β	log K_1	log K_2	log K_3	log β
—	7.19	5.29	5.02	17.50	6.54	5.64	5.32	17.50	6.74	5.84	5.67	18.25	6.69	6.24	5.82	18.75
4-Methyl	6.96	5.41	5.14	17.51	6.63	5.67	5.29	17.68	6.66	5.91	5.69	18.26	7.16	6.41	6.14	19.71
4-Chloro	7.21	5.06	4.93	17.19	6.51	5.71	5.53	17.74	6.66	6.21	5.88	18.74	6.66	6.21	5.88	18.74
4-Bromo	5.62	4.62	4.44	14.68	6.0	5.37	5.24	16.61	6.37	5.24	5.14	16.93	6.37	5.92	5.54	17.83
	GdL_3				TbL_3				YL_3				YbL_3			
	log K_1	log K_2	log K_3	log β	log K_1	log K_2	log K_3	log β	log K_1	log K_2	log K_3	log β	log K_1	log K_2	log K_3	log β
—	6.79	6.14	5.92	18.85	7.14	6.14	5.97	19.25	7.44	6.29	6.22	19.95	7.89	6.84	6.69	21.42
4-Methyl	7.16	6.11	5.66	18.93	7.26	6.31	6.14	19.71	7.16	6.51	6.09	19.76	8.56	6.96	6.64	22.16
4-Chloro	6.67	6.00	5.53	18.20	7.06	6.31	6.03	19.40	6.76	6.41	5.98	19.14	7.31	6.71	6.58	20.60
4-Bromo	6.37	5.92	5.54	17.83	6.47	6.02	5.64	18.13	6.57	6.02	5.64	18.23	7.17	6.77	6.44	20.38

This may be due to the strong hydrogen bonding in the hydroxamic acid moiety



which restricts the movement of the rest ($CH_3.CO.CH_2$–) of the molecule.

Further the methylene protons shows a quartet characteristic of geminal coupling and the coupling constant J_{AB} is of the order of 15–18 Hz. In addition to that, the signal due to the hydroxyl proton (marked H*) disappears on the addition of D_2O.

It is evident from the above, that the compounds studied here behave as bidentate rather than terdentate ligands towards metal ions. Further, the elemental analyses of the isolated copper complexes show the metal:ligand ratio of 1:2, indicating a co-ordination number of 4.

We have found from the titration data and formation curves that the maximum $\bar{n}$ values reached lie in the range 2–2.5 for bivalent and tervalent metals, respectively, demonstrating 1:2 and 1:3 complex formation in solution.

The elemental analyses and infrared spectra of the ligands and complexes are summarized in Table 3. The band due to the C=O stretching vibrations in all the ligands is displaced towards longer wavelengths on complex formation. This indicates co-ordination of the carbonyl oxygen atom to the metal. If the structures of the complexes are comparable, the greater the displacement of this band, the stronger the C=O → M bond.[8] The displacements found are of the order of 85–100 cm^{-1}, indicating very strong chelation. The bands due to hydroxyl stretching vibrations, which appear in the range 3300–3250 cm^{-1} in all the ligands, were not found in the complexes, because of N–O → M bond formation.

The pK values of the ligands show that the substituents on the phenyl ring have a marked influence on the electron density at the nitrogen atom as well as on the reactivity of the donor atoms. The pK values are in the order (indicated by substituent group) F < Cl < Br < H < CH_3. From Tables 4 and 5 it is clear that the stability constants of the complexes increase with the basic strength of the ligands since the ligands studied here are structurally similar. The values of the stability constants of copper, nickel and manganese follow the expected order given by Mellor and Maley[9] and merit no further attention.

All the ligands mentioned in Table 1 are soluble in 70% dioxan/water mixture, except **VII** and **VIII**, which cannot be studied in the same way as the others.

The stability constants of the lanthanide complexes increase fairly regularly with decrease in ionic radius, with the gadolinium complex being less stable than predicted from ionic considerations. The curve of log β *vs.* e/r, as shown in Fig. 1 for the 4-bromo-*N*-hydroxyacetoacetanilide complexes of the lanthanides is reasonably linear.

The differences between the three stability constants K_1, K_2 and K_3 are not marked, suggesting that there is almost equal tendency for the formation of the neutral complex species LnR_3 as for LnR^{2+}. The comparison of the stability constants of these complexes with those for complexes of other oxygen-donor ligands such as acetylacetone and benzoylphenylhydroxylamine in the same solvent mixture, suggests that, if the physical characteristics of the precipitate are satisfactory, *N*-hydroxyacetoacetanilide and its derivatives might be as successful as ligands such as benzophenylhydroxamic acid for the gravimetric determination of lanthanides.[10]

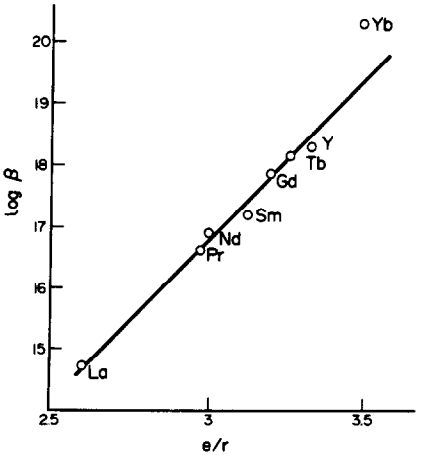


Fig. 1. Plot of log β *vs.* e/r of 4-bromo-*N*-hydroxyacetoacetanilide complexes of lanthanides.

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A CASE STUDY OF THE AMBIENT OXIDATION OF TWO ZINC–LEAD (SULPHIDE) REFERENCE ORES

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Summary—The history of two lead–zinc (sulphide) reference ores is presented to show quantitatively the serious effects of ambient oxidation on unprotected samples. This study should serve as a warning to the users and producers of sulphide-bearing reference ores and concentrates. Suggestions are given for overcoming or diminishing the oxidation problem.

There is wide-spread concern among ore analysts that "in-house" and "certified" reference ores and concentrates containing sulphide minerals can undergo a change in composition due to oxidation during storage and use under laboratory conditions. Yet there seems to have been no systematic quantitative study intended to expose the magnitude of the problem for types of sulphide ore commonly used for reference purposes. It is, therefore, considered useful to document a study made in the Canadian Certified Reference Materials Project (CCRMP), of the history of two complex zinc (sphalerite) reference ores, MP-1 and KC-1, that have been affected by oxidation. It is hoped that users and potential producers of similar reference materials will benefit from it.

Although the potential danger of oxidation of MP-1 and KC-1 was recognized in the CCRMP at the outset, it was thought reasonable to expect long-term stability for dry reference ores stored in well-capped bottles. As part of a general study of the factors affecting the stability of sulphide ores Steger[1] determined certain oxidation products in samples of MP-1 and KC-1 that had been exposed to air at various relative humidities and temperatures for periods up to seven weeks. The results of his work indicated that both MP-1 and KC-1, kept in well-sealed bottles, should not undergo significant oxidation and concomitant change in overall composition during their expected life in storage or during exposure to the atmosphere during the taking of subsamples.

However, in mid-1976, analyses by the widely-used EDTA method,[2] of arbitrarily selected bottles of MP-1 and KC-1 that had been in use in certain CANMET and commercial laboratories for several years, yielded total zinc values that were less than the original lower 95% confidence limits of 16·20% and 20·31% respectively (see Table 6). These confidence limits were derived from zinc results obtained largely by the titrimetric ferrocyanide method and by atomic absorption; however, some were obtained by the EDTA method.

Because of the possibility that the current zinc results by the EDTA method were biased with respect to the original recommended zinc values, the EDTA method was thoroughly assessed experimentally at CANMET and found not to lead to low results when applied to materials such as MP-1 and KC-1. Therefore, it was concluded that alteration of the selected samples had indeed occurred.

This paper presents analytical data that show the change in composition, due to oxidation, of bottled samples of MP-1 and KC-1 which had been stored and opened from time to time in the laboratory and also of unopened bottles of the reference ores which had been in storage at CANMET since their certification. Suggestions are made that might help producers and users of sulphide-bearing reference ores to avoid or diminish the danger of oxidation changes in such certified reference materials.

Description of reference ores MP-1 and KC-1

The approximate chemical composition, mineralogical composition and particle size analyses for MP-1 and KC-1 are given in Tables 1, 2 and 3 respectively. It is of interest to note that a much larger proportion of MP-1 than of KC-1 is in the $<37\,\mu m$ fraction. Image (size) analysis has shown that the relative fineness of sphalerite, pyrite and chalcopyrite is similar for MP-1 and KC-1 in the $<37\,\mu m$ fraction. However, galena in this fraction is finer in KC-1 than in MP-1.

Certification of MP-1 and KC-1 as compositional reference materials

The preparation and certification of MP-1 and KC-1 for selected constituents is described in certification documents[3,4] which are issued to users of the

Table 1. Approximate chemical composition of MP-1 and KC-1

Constituent	MP-1 %	KC-1 w/w
O	27	14
Si	19	11
Al	4	0.8
Fe	6	16
Mg	0.05	0.05
Ca	3	0.3
K	0.1	0.1
Na	0.01	0.2
Ti	0.1	—
Mn	0.05	0.05
S	12	28
C	0.1	0.2
Zn	16.33*	20.37*
Pb	1.93*	6.98*
Cu	2.15*	0.11*
Sn	2.50*	0.68*
Ag	59.5 ppm*	0.11*
As	0.79*	—
In	0.071*	—
Bi	0.025*	—
Mo	0.015*	—
Cd	0.07	—
W	0.02	—
H_2O lost at 980°C	1.6	0.7
Moisture (2 hr at 105°C)	0.2	0.1

* Recommended value in 1972 (MP-1) or 1974 (KC-1).

Table 2. Mineralogical composition of MP-1 and KC-1

Minerals	MP-1 %w/w	KC-1 %w/w
Sphalerite	25.1	32.7
Galena	2.2	8.8
Chalcopyrite	3.8	0.3
Pyrite	1.3	29.9
Arsenopyrite	1.7	—
Pyrrhotite	—	0.3
Stannite–kesterite	2.9	—
Molybdenite	0.02	—
Tetrahedrite + stephanite	0.05	—
Cassiterite	2.0	0.9
Wolframite	0.04	—
Bismuth	0.03	—
Silver	—	0.1
Quartz	34.7	20.6
Chlorite	7.0	0.9
Feldspar	0.8	5.0
Fluorite	6.6	—
Siderite	—	0.4
Topaz	6.1	—
Kaolinite	5.8	—
Rutile	0.05	—

reference ores but are not otherwise readily available. Therefore, a brief account is given of the procedures used in the Canadian Certified Reference Materials Project to produce reference ores and related materials.

The finely ground, homogenized ore materials are packaged in 100- or 200-g units. Two randomly-selected bottles are sent to each laboratory participating in the interlaboratory certification programme (there are usually more than fifteen). For each constituent to be certified five replicate determinations are requested for each bottle. This scheme permits the computation of the between-bottles variance and the average within-laboratory variance, as well as the ultimate confirmation of the homogeneity of the reference material.[5,6] In most interlaboratory programmes of the CCRMP, contributors use methods of their choice and provide methodological details so that analytical results can be scrutinized for chemically explainable outliers. To establish whether the overall mean (consensus) value for each selected constituent should be given the status of a recommended and certified value, a criterion of quality called the "certification factor" is used.[5] The certified values originally assigned for MP-1 and KC-1 are given in Table 6.

Effect of ambient oxidation of "in-use" bottles of MP-1 and KC-1

Table 4 gives zinc values for arbitrarily selected bottles of MP-1 and KC-1 that had been opened for analysis at various times in their history and were kept under laboratory conditions without special protection from oxidation between openings. The values are, in most cases, the means of five or more replicate determinations on material from bottles, the contents of which had been well mixed before the taking of subsamples. As Table 4 shows, the precision of the means is not a function of age of the samples, and so the question of sample heterogeneity was not given special consideration in this study.

Even though the results have been obtained by a number of analysts using different methods and working in different laboratories, it is clear that in all cases except that of sample D there is a marked decrease in total zinc content with increasing age of the reference material. Even in the absence of additional evidence, which is given below, it would be safe to assume that the change in composition was due to the oxidation of sulphide minerals, mainly to sulphates.[7]

Although the details of use and the storage conditions of temperature, relative humidity and corrosiveness of the atmosphere in a particular laboratory cannot be specified, the results in Table 4 strongly suggest that the extent of oxidation is dependent upon such conditions. For example, samples E and G of MP-1 and KC-1 respectively, held by commercial laboratory No. 2, suffered appreciably greater change

Table 3. Particle size analysis* of MP-1 and KC-1

Mesh size (μm)	MP-1	KC-1
>74	0.4	1.7
46–74	10.7	62.4
37–46	8.1	11.8
<37	80.8	24.1

* Wet-screen method.

Table 4. Correlation of zinc values with history of selected samples of MP-1 and KC-1

Sample	Date of analysis	Zn, % w/w	s, % w/w	Method, laboratory and analyst
			MP-1	
A	Jan. 1972	16.17 (5)†	0.047	Titrimetric, EDTA; Commercial Lab 1*
	June 1976	16.01 (5)	0.014	Titrimetric, EDTA; CANMET, Analyst 1
	Nov. 1976	15.91 (5)	0.012	Titrimetric, EDTA; CANMET, Analyst 2
B	Jan. 1972	16.15 (5)	0.036	Amperometric, ferrocyanide, CANMET*, Analyst 3
	Aug. 1973	16.15 (5)	0.026	Titrimetric, EDTA; CANMET, Analyst 3
	June 1976	16.04 (5)	0.031	Titrimetric, EDTA; CANMET, Analyst 1
	Nov. 1976	15.94 (5)	0.011	Titrimetric, EDTA; CANMET, Analyst 2
	Oct. 1977	15.74 (5)	0.090	Amperometric, ferrocyanide, CANMET, Analyst 3
C	June 1976	16.02 (5)	0.025	Titrimetric, EDTA; CANMET*, Analyst 1
	Nov. 1976	15.99 (5)	0.011	Titrimetric, EDTA; CANMET*, Analyst 2
D	Nov. 1976	15.86 (5)	0.025	Titrimetric, EDTA; Commercial Lab 1*
	Mar. 1977	15.87 (5)	0.020	Titrimetric, EDTA; CANMET, Analyst 2
E	Sept. 1971	16.30 (5)	0.030	Polarographic; Commercial Lab 2*
	Dec. 1976	15.53 (10)	0.042	Polarographic; Commercial Lab 2*
	Mar. 1977	15.57 (5)	0.008	Titrimetric, EDTA; CANMET, Analyst 2
			KC-1	
F	Jan. 1974	20.22 (5)	0.026	Titrimetric, EDTA; CANMET, Analyst 1
	Oct. 1976	20.03 (5)	0.012	Titrimetric, EDTA; CANMET, Analyst 1
	Nov. 1976	20.12 (3)	0.032	Titrimetric, EDTA; CANMET, Analyst 2
G	Jan. 1974	20.63 (5)	0.089	Polarographic, Commercial Lab 2*
	Dec. 1976	19.98 (10)	0.079	Polarographic, Commercial Lab 2*

† Number of replicate determinations.
* Indicates laboratory where bottle was opened originally.

than did corresponding samples B and F held by CANMET (see Fig. 1).

Analytical verification of oxidation of sulphides

The concentration of leachable metal(s) in a sulphide ore is an excellent indicator of the extent of oxidation. Reliable methods for determining zinc, lead and copper as oxidation products of sphalerite, galena and chalcopyrite in ores and related materials have been developed recently at CANMET[8,9] and these were applied to various samples of MP-1 and KC-1, for which the total zinc values were determined at essentially the same time as the metals in oxidation products, hereafter referred to as "oxidized metals". This latter parameter, when compared with the original zinc value assigned at the time of certification, also gives a direct measure of the overall change in composition due to oxidation.

These oxidized-metal concentrations and the original certified zinc values for MP-1 and KC-1 were used to calculate the fraction of the total zinc, lead and copper contents that had been oxidized. In Fig. 1 the results are plotted against the current total zinc content of the test samples. Although the rate of oxidation of the test samples varied with conditions of use and storage, the linearity of the plots in Fig. 1 confirms the validity of this method of estimating the degree of oxidation of a sample to produce oxidized lead, -zinc, or -copper.

The difference in slope of the curves in Fig. 1 indicates that for a given set of conditions the rate of oxidation of the sulphides is galena > sphalerite >

Table 5. Calculated weight gains total zinc values of MP-1

Sample	Gain in weight, *mg/g*				Total Zn, %	
	ZnS	$FeCuS_2$	PbS	Total	Calcd.	Found
B	24.6	2.2	0.4	27.1	15.90	15.99
C	22.1	1.9	0.3	24.4	15.94	15.94
D	29.4	3.0	1.0	33.4	15.90	15.86
E	53.0	7.3	1.1	61.5	15.38	15.53
1	23.8	2.1	0.9	26.8	15.90	15.99
2	35.3	3.2	0.6	39.1	15.71	15.79
3	28.0	3.0	0.5	31.5	15.83	15.89
4	13.0	1.0	0.3	14.3	16.10	16.14

Samples 1–4 are additional to those described in the text and Table 5.

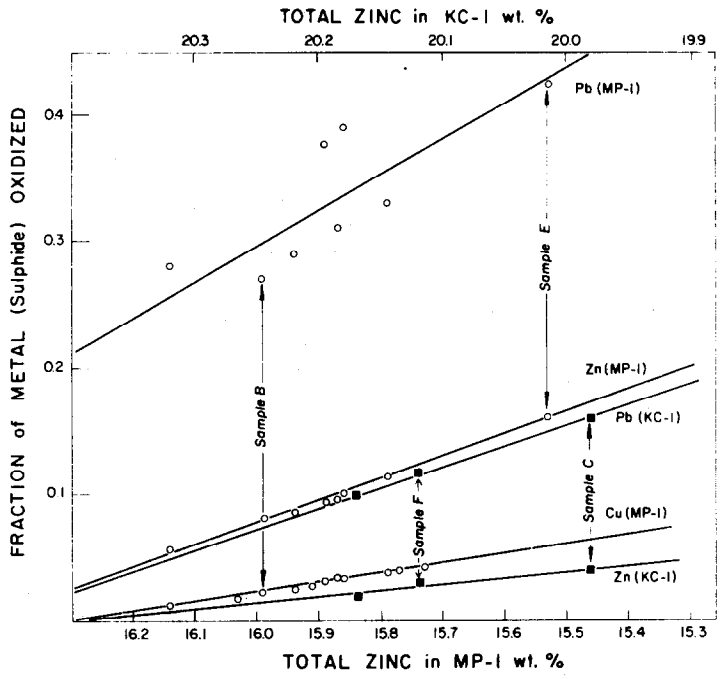

Fig. 1. Correlation of extent of oxidation of sulphides of zinc, lead and copper with total zinc in MP-1 and KC-1. Note: slopes of plots have slight negative error (max 5%) because oxidized metal values were determined on samples that had been partially oxidized since certification.

chalcopyrite in MP-1 and KC-1. That the slopes of the MP-1 plots are higher than the corresponding ones for KC-1 probably reflects the higher proportion of < 37-μm material in MP-1, as well as differences in composition of the corresponding minerals and the overall mineral assemblage of the ores.

Interestingly, the intercepts of the plots in Fig. 1 should be a measure of the extent of oxidation of the base-metal sulphides, which was not determined at the time of certification, *i.e.*, 1972 for MP-1 and 1974 for KC-1. For oxidized zinc, copper and lead in MP-1, the values were calculated to be 3.9, 0 and 4 mg/g, respectively, by linear regression. The chalcopyrite in MP-1 was evidently insignificantly oxidized at the time of certification. A similar observation can be made for the sphalerite in KC-1.

Physical mechanism of oxidation

It is evident from the foregoing that the liner of the bakelite caps on the bottles of MP-1 and KC-1 did not provide an air-tight seal and that significant oxidation of sulphide minerals occurred. Although the chemical mechanism of the oxidation has not been completely elucidated, it is known that the principal oxidation products are metal sulphates,[7] *e.g.*,

$$ZnS + 2O_2 + 7H_2O \rightarrow ZnSO_4 \cdot 7H_2O$$

$$PbS + 2O_2 \rightarrow PbSO_4$$

$$4FeCuS_2 + 15\tfrac{1}{2}O_2 + 25H_2O \rightarrow 4CuSO_4 \cdot 5H_2O + Fe_2(SO_4)_3 \cdot 5H_2O + Fe_2O_3 + S$$

For a particular sample, the expected gain in weight due to the oxidation of each sulphide mineral can readily be calculated from the difference between the current oxidized metal content and that at the time of certification (values given above). The calculated gain in weight due to the oxidation of sphalerite, galena and chalcopyrite, the total gain in weight, the expected total Zn value given by the certified value divided by the new weight and the total Zn values determined are shown in Table 5. The calculated total Zn values are all approximately 0.1–0.2% (absolute) lower than the values determined. The change in the calculated values, however, is in good agreement with that for the determined values. Possible reasons for the lower calculated total Zn values are as follows. The values for the oxidized metal at the time of certification are obtained by extrapolation of the data and thus could be in error. This would certainly be the case if the oxidation kinetics were non-linear. It has been assumed that the zinc sulphate is the heptahydrate, but it is possible that the degree of hydration could vary with the thickness of the layer produced. The occurrence of the pentahydrate in the oxidation products of chalcopyrite has been demonstrated.[7]

These two sources of error can easily be overcome if the total Zn values are calculated by using the data for any one of the analysed bottles. For example, if the data for Bottle B are used as the basis for calculations, the calculated total Zn values for the other bottles are given by $(15.99 \times 1.0329)/[1 +$ total gain in weight (mg/g)]. The calculated total Zn values for Bottles B, C, D, E, 1, 2 and 3 would be 15.99, 16.04, 15.88, 15.39, 16.00, 15.91 and 16.24, respectively, in

excellent agreement with the total Zn values found and showing that the oxidized metal values are a good indicator of the extent of oxidation. Comparable data were not sought for KC-1.

The larger degree of scatter for oxidized-lead compared with that for zinc or copper for MP-1 in Fig. 1 can be explained as follows. The total zinc value is obviously fixed, but its concentration is dependent on the gain in weight due to oxidation of the ore. The results in Table 5 show that it is the oxidation of sphalerite that makes the largest contribution to the gain in weight of the ore. (Note that pyrite is in low concentration in MP-1.) Therefore, Fig. 1 is, in effect, a plot of the fraction of metal species oxidized *vs.* the gain in weight (due essentially to the oxidation of sphalerite). It is evident that the plot for oxidized zinc should be linear with a low degree of scatter.

The oxidation of sphalerite must, in general, be accompanied by the oxidation of galena and chalcopyrite, so the plot of oxidized lead and copper against the gain in weight due to the oxidation of sphalerite might also be linear, as observed. Appreciable scatter for the oxidized-lead and oxidized-copper plots could easily be explained by the dependence of the rate of oxidation of galena and chalcopyrite on temperature and relative humidity being different from that of sphalerite. The conditions of temperature and relative humidity to which MP-1 and KC-1 were exposed must have varied from bottle to bottle in order to account for the different extents of oxidation. Any variation in oxidation conditions would be more important for galena, which shows the greatest tendency towards oxidation, so a plot of oxidized-lead *vs.* gain in weight due to sphalerite oxidation could, as is observed, show appreciable scatter.

The linear relationship between oxidized-lead or oxidized-zinc values and the total zinc value for KC-1 in Fig. 1 cannot be as easily rationalized as that for MP-1, because it is not known if the change in total zinc value is essentially a result of the gain in weight due to the oxidation of sphalerite, as is the case for MP-1. KC-1 contains approximately 30% pyrite which probably also undergoes oxidation. Unfortunately, there is no analytical method for determining oxidized iron derived from iron sulphides when galena, sphalerite, *etc.*, are present; thus, the bottle-to-bottle variation of oxidized iron is not known for KC-1.

The three data points for KC-1 in Fig. 1 indicate a linear relationship between oxidized metal value and total zinc value, which suggests that either pyrite is not oxidized under the ambient conditions, or is oxidized, but to an extent proportional to that observed for galena and sphalerite. Any comment on possible differences in the oxidation rates of pyrite, galena and sphalerite due to differences in temperature or relative humidity would not be justified on the basis of the limited data available for KC-1.

Figure 2 is a plot of the change in weight of 200-g samples of MP-1 and KC-1 that were deliberately exposed to the atmosphere in their storage room for 15 min during each month of 1977 and part of 1978, the ambient air temperature varying from 20° to 28° during the period. Also shown in Fig. 2 is the mean monthly relative humidity for the same period,

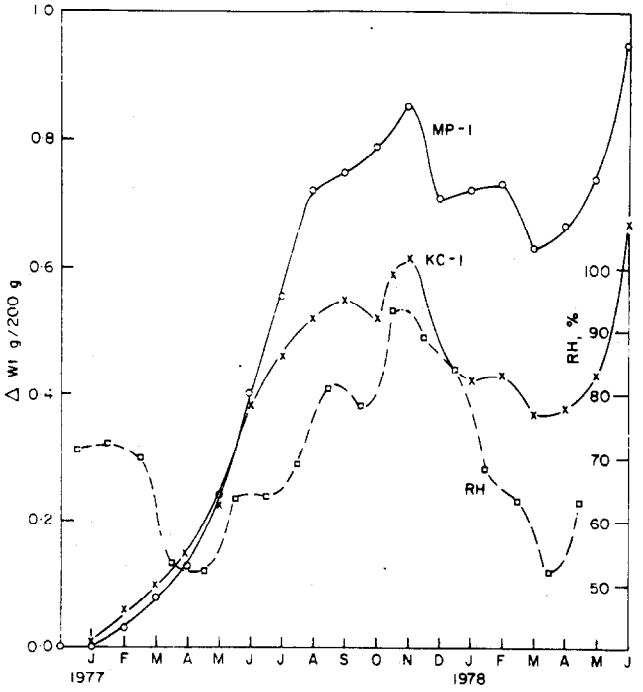

Fig. 2. Weight change of 200-g samples of MP-1 and KC-1 exposed to atmosphere for 15 min each month throughout 1977 and early 1978. Also shown is relative humidity (RH) measured at Ottawa airport.

Table 6. Revised and original means for zinc and their precision

	Zn, % w/w	95% Confidence limits, % w/w	Average within-lab coefficient of variation, %	Certification factor
MP-1				
1972 original values	16.33	16.20–16.45	0.46	3.36
1977 revised values	15.90	15.84–15.96	0.42	1.74
KC-1				
1974 original values	20.37	20.31–20.43	0.38	1.61
1977 revised values	20.07	20.01–20.14	0.26	2.55

measured at the Ottawa International Airport. Although the atmospheric conditions in the laboratory building where the reference materials are stored would be different from those out of doors, especially during the winter months, there is, nevertheless, a good correlation between the weight change and the relative humidity at the airport. No doubt the net gain in weight in 1977 of 0.4% and 0.2% respectively for the test bottles of MP-1 and KC-1 was mainly due to oxidation, the rate of which was largely controlled by humidity. Interestingly, test bottles of MP-1 and KC-1 which were never opened and had their caps tightly taped with friction tape, gained 0.2% and 0% in weight during 1977. The problem of effectively sealing containers of sulphide ores will be discussed below.

Recertification of MP-1 and KC-1[10]

Although peripheral to the current study, the following is of interest to potential users of MP-1 and KC-1.

In mid-1977 an interlaboratory programme was undertaken to determine whether the never-opened stock of MP-1 and KC-1 should continue to be distributed to users after revision of values for zinc and other constituents. Some 50 randomly-selected bottles of each reference ore were analysed for zinc, mainly by the EDTA method. A statistical evaluation of the results indicated that bottle-to-bottle homogeneity had remained satisfactory and that a new recommended zinc value could be assigned for both reference ores. Table 6 gives the revised and original means and shows that the precision of the 1977 results is as good as, or better than the original. The low certification factors[5] also confirm the acceptability of the new means.

The ratio of the new zinc value to the original value is 0.974 and 0.985 for MP-1 and KC-1 respectively. These ratios have been used to "correct" the original certified values for constituents other than zinc. The revised values and their corrected 95% confidence limits are given in Table 7. Justification for revising the confidence limits is based on the fact that the homogeneity of the ores has not been affected by oxidation; hence it is assumed that the precision of the original results still applies.

Packaging of reference ores—recommendations

Laminated polyester–aluminium foil–polyethylene pouches are commonly used to protect foodstuffs effectively from the atmosphere. The application of such foil pouches to the prevention of atmospheric oxidation of sulphide-bearing reference materials seemed promising; therefore, some experiments were

Table 7. Recommended (1978) values and confidence limits for selected constituents in MP-1 and KC-1

Constituent	Recommended value % w/w	95% Confidence limits, % w/w
	MP-1	
Zn	15.90	15.84–15.96
Sn	2.43	2.32–2.54
Cu	2.09	2·06–2·12
Pb	1.88	1.85–1.91
Mo	0.014	0.013–0.015
In	0.069	0.066–0.072
Bi	0.024	0.022–0.026
As	0.77	0.75–0.79
Ag	57.9 ppm	55.7–60.1 ppm
	KC-1	
Zn	20.07	20.01–20.14
Pb	6.87	6.83–6.91
Sn	0.67	0.66–0.68
Cu	0.112	0.110–0.114
Ag	0.112	0.110–0.114

performed to test the protective properties of a typical laminated foil (0.0005 in. thick, *i.e.*, about 12.5 μm).

The bottles used in the CCRMP for packaging reference ores have the customary bakelite caps with glazed cardboard liners. It was demonstrated that heated capped bottles leaked substantially when immersed in cold water, because of the pressure difference that was generated. However, insertion of a disc of laminated foil over the cardboard liner essentially eliminated such leakage.

In other experiments, a test piece of the laminated foil was found to sustain a vacuum of 20 μm of mercury or better, and a heat-sealed pouch containing hydrogen sulphide as an olfactant did not leak detectably during a test period of four months.

As a consequence of these tests, all bottles of MP-1 and KC-1 in stock at CANMET were fitted with a foil liner in the cap and then sealed, under nitrogen, in laminated foil pouches. Because of the high probability that these measures will be effective in ensuring the long-term stability of the ores and because of the substantial demand for them, they will continue to be issued to users. As a precaution, test bottles will be monitored periodically for change in composition.

In view of the findings described in this paper, it is strongly recommended that containers of sulphide-bearing reference materials should be stored under dry nitrogen. Also, when subsamples are taken, the contents of bottles should be exposed to air for the shortest time possible.

No doubt a few bottles of reference materials can be stored conveniently under nitrogen in a desiccator. However, in consideration of the ready availability and relatively low cost of foil pouches and "thermo-jaw" sealing devices, it may be practicable to reseal containers of reference materials after each use, especially in laboratories where large numbers of reference materials are required.

Because interlaboratory certification programmes may last a year or more, it is important that programme co-ordinators distribute samples of candidate reference materials that have been well protected from oxidation during storage and shipment to participants and that they instruct participants to follow the procedures outlined above.

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EXTRACTIVE SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF TUNGSTEN AS FERROCYANIDE

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Summary—Tungsten, in amounts ranging from micrograms to milligrams, can be extracted into isoamyl alcohol, as the tungsten(V) ferrocyanide complex obtained by reduction of tungsten(VI) with tin(II) in 4*M* hydrochloric acid containing ferrocyanide. It can thus be separated from iron, cobalt, chromium, manganese, arsenic, antimony, bismuth, silicon, calcium and copper, their precipitation being prevented by addition of glycerol and, in the case of iron, sulphosalicyclic acid. Molybdenum, vanadium and nickel are not separated from tungsten, however. Tungsten can also be determined spectrophotometrically as tungsten(V) ferrocyanide. The absorbance of the brown complex is measured in aqueous solution or preferably after extraction into isoamyl alcohol. As many alloying elements interfere, they should be separated by the ferrocyanide extraction or other suitable method. Both the separation and the determination methods give satisfactory results with an overall error of not more than 0.5% in the analysis of practical samples containing low or high percentages of tungsten.

The colour reaction with ferrocyanide has long been used for detection of traces of tungsten.[1] The reaction has also been proposed for determination of milligrams of tungsten by measurement of the absorbance at 480 nm but is rather slow.[2] A later modification[3] makes the measurement at 377 nm but the colour is unstable and obeys Beer's law only approximately. As ferrocyanide precipitates many cations,[4] their prior separation becomes necessary, further limiting the use of the method.

We have found that $Fe(CN)_6^{4-}$ is extractable as an ion-association complex into isoamyl alcohol as might be expected on analogy with $Fe(SCN)_4^-$ and $FeCl_4^-$.[5] The results of our study for separation and determination of tungsten by extraction as ferrocyanide are presented below.

EXPERIMENTAL

Reagents

Tungsten solution. Sodium tungstate was dissolved and the solution was standardized[6] titrimetrically with iron(III) and then diluted as required.

Potassium ferrocyanide solution. 5%.

Stannous chloride solution, 100% w/v in concentrated hydrochloric acid.

Isoamyl alcohol. The fraction boiling at 128–132° was used.

Samples

Industrial samples. Ferrotungsten A and B (100 mg) were opened out by standard methods[7] and made up to 100 ml, and suitable aliquots were taken for analysis.

Synthetic samples. These were prepared by mixing solutions of the ions to give the compositions shown in Table 5.

Separation of tungsten by extraction as ferrocyanide

To the slightly alkaline sample solution add either 0.3 g of tartaric acid for up to 10 mg of tungsten or 10 ml of glycerol for up to 20 mg, followed by 1 ml of stannous chloride solution and enough conc. hydrochloric acid to make the total acidity 5*M* in a final volume of 16 ml. Heat just to the boil, immediately add 4 ml of potassium ferrocyanide solution and cool to room temperature. For less than 3 mg of tungsten add 1 ml of stannous chloride solution to the alkaline sample, followed immediately by 4 ml of potassium ferrocyanide solution and enough hydrochloric acid to make the total acidity 4*M* in a final volume of 20 ml. Heated just to the boil and cool to room temperature.

Transfer the cold brown solution quantitatively to a 100-ml separating funnel with 5 ml of 4*M* hydrochloric acid. Shake for 30 sec with 20 ml of isoamyl alcohol. Separate the layers. Add 1 ml of potassium ferrocyanide solution to the aqueous phase, heat just to the boil, cool and again extract for 30 sec with 5 ml of isoamyl alcohol. When glycerol is used, add 0.5 g of boric acid to the aqueous phase after the first extraction and repeat the second extraction. The combined solvent phases contain all the tungsten.

Modification for other elements. When cobalt, copper and chromium are present with $\leqslant$20 mg of tungsten, add 10 ml of glycerol and, if iron is present, sulphosalicyclic acid (about 100 mg for up to 50 mg of iron) to the alkaline sample solution, and proceed as in the first method above, using 20, 5, 5 and 5 ml of solvent. Extraction of tungsten is almost quantitative, but only 99.3% in presence of cobalt and of copper.

Back-extraction of tungsten. Equilibrate the combined solvent phases, for 1 min each time, first with 20 ml of sodium hydroxide solution, concentrated enough to keep tin in solution as stannate and to give rapid separation of the layers, and then twice with 10-ml portions of water containing 3 or 4 drops of saturated sodium hydroxide solution. To the combined back-extracts add saturated sodium hydroxide solution dropwise to redissolve any precipitated tin hydroxide. Heat to the boil, filter off any hydroxide precipitate on a Whatman No. 41 paper, make up to a suitable volume and determine tungsten directly or in an aliquot.

Spectrophotometric determination of tungsten as ferrocyanide

To a sample solution containing not more than 1400 μg of tungsten add 0.1 g of tartaric acid, followed by 1.5 ml of stannous chloride solution and enough conc. hydro-

chloric acid to give a total acidity of 5*M* in a final volume of 16 ml. Heat just to the boil, add 4 ml of potassium ferrocyanide solution, boil for 5–6 min and cool. Transfer quantitatively to a separating funnel with 5 ml of 4*M* hydrochloric acid, and equilibrate for 30 sec with 20 ml of isoamyl alcohol. Pass the extract through a dry Whatman No. 41 paper and make up to 25 ml in a standard flask. Measure the absorbance in a 1-cm cell, against isoamyl alcohol, at 490 nm.

RESULTS AND DISCUSSION

Extractive separation of tungsten as ferrocyanide

The reaction with ferrocyanide has long been used for detection of tungsten, but has not received much attention for its determination, separation or extraction. It is found that tungsten(VI) can be extracted as the yellow ferrocyanide from hydrochloric acid medium. From 10 mg of tungsten(VI) taken in 20 ml of 2*M* and 5*M* hydrochloric acid, isoamyl alcohol extracts about 80 and 96% respectively, but the solvent phase remains slightly turbid. With pure tributyl phosphate the extraction is quantitative and the solvent phase remains clear.

The brown tungsten(V) ferrocyanide is also found to be extractable into oxygenated solvents but not into amines and non-polar solvents. In a single extraction, isoamyl alcohol gives almost quantitative removal without any turbidity; isoamyl acetate and methyl isobutyl ketone give partial separation. With ether a dense precipitate is formed. The free reagent is also extracted almost quantitatively (presumably as ferrocyanic acid) into isoamyl alcohol. Various parameters influencing the extraction of tungsten(V) ferrocyanide are shown in Table 1. The extraction with isoamyl alcohol remains nearly constant at acidities from 4 to 7*M*; with $< 4M$ acid the tin precipitate does not redissolve. The extraction increases with volume of ferrocyanide solution up to 4 ml and remains constant up to 6 ml in 25 ml solution. It decreases if more than 1 ml of tin(II) chloride solution is used. The optimum conditions give 99.0% extraction in a single operation. Repetition of the extraction on the aqueous phase is not effective (owing to the almost complete extraction of the excess of ferrocyanide), unless 1 ml of ferrocyanide solution is added and the solution is boiled and cooled. If the amount of tungsten is >3 mg it is precipitated as the ferrocyanide but up to 10 mg can be kept in solution with tartaric acid and up to 20 mg with glycerol.

Effect of diverse ions. Tartaric acid, sodium chloride and acetate do not affect the extraction but sodium citrate, sulphate, phosphate and oxalate decrease the extraction in that order (Table 2).

In the amounts usually present, arsenic, antimony, bismuth, calcium, manganese and silicate have practically no effect on the extraction of tungsten and are themselves only slightly extracted (Table 3). In the absence of glycerol, iron, nickel, cobalt, chromium, molybdenum, vanadium and copper are precipitated as ferrocyanide under the chosen conditions and co-precipitate 25–40% of the tungsten present, probably by formation of ternary complexes. Addition of 10 ml of glycerol to 25 ml of the final sample solution, before any of the other reagents, prevents the precipitation of cobalt, copper and chromium as ferrocyanides, but their presence decreases the extraction of tungsten by about 28, 28 and 15% respectively. Iron can be masked with sulphosalicylic acid but a blue precipitate (tungsten blue) appears, and though it can be kept in solution with glycerol, the extraction of tungsten is decreased by nearly 15%. In presence of glycerol molybdenum also is not precipitated but is almost quantitatively extracted as the brown molybdenum(V) ferrocyanide. On the other hand nickel and vanadium ferrocyanides are still precipitated. Glycerol itself decreases the extraction of tungsten by about 9%. Hence when it is used, after the first extraction the excess of glycerol is masked by warming with 0.5 g of boric acid until dissolution is complete, and three further extractions are done, each with 5 ml of solvent after addition of 1 ml of ferrocyanide solution, boiling and cooling to room

Table 1. Effect of various parameters on the extraction of tungsten(V) ferrocyanide*

Acidity (*M* HCl)	4	5	6	7	
Extraction† (% W)	85.2	85.1	85.1	85.0	
$SnCl_2 \cdot 2H_2O$ soluti((ml)	1	2	3	4	
Extraction† (% W)	85.1	83.5	81.9	80.2	
$K_4[Fe(CN)_6]$solutic (ml)	1	2	3	4	5
Extraction†§ (% W)	85.1	93.5	94.3	99.0	99.0

* Except for the individual variations shown, the conditions were: 5*M* hydrochloric acid, 1 ml of stannous chloride solution, 1 ml of ferrocyanide solution, 20 ml of each phase, 1.6 mg of tungsten.

† By difference; W determined in the aqueous phase by Hg–SCN method[8].

Table 2. Effect of anions on the extraction of tungsten(V) ferrocyanide*

Salt added	Amount g/25 ml	Extraction,†%
—	—	99.0
Sodium chloride‡	0.5	98.9
Sodium sulphate‡	0.5	95.0
Sodium phosphate‡	0.5	94.4
Tartaric acid‡	0.1	99.0
Sodium acetate§	0.1	99.1
Sodium oxalate§	0.1	94.5
Sodium citrate§	0.1	98.5

* Tungsten 2 mg/25 ml; modified extraction procedure.
† By difference; tungsten determined in the aqueous phase by Hg–SCN method.[8]
‡ Added before reduction.
§ Added after reduction.

temperature. However, only two extractions in all are needed, if glycerol is not used.

Spectrophotometric determination of tungsten as ferrocyanide

The brown tungsten(V) ferrocyanide complex is obtained by adding all the reagents (stannous chloride, ferrocyanide and acid in that order) to the sample solution and heating just to the boil. The absorbance of the complex is influenced by various parameters. Complex formation starts at 3.5*M* hydrochloric acid concentration, the absorbance increasing with acid concentration up to 4.5*M* and then decreasing slightly at higher concentration (up to 6*M*) (Fig. 1, curve A); the colour changes to yellow at higher acidities (shown by dotted line). The absorbance increases with volume of ferrocyanide solution up to 4 ml (curve B), of stannous chloride up to 1.5 ml (curve C), remaining almost constant for up to 5 ml in both cases. Maximum absorbance is obtained in 10 min after addition of the reagents and then remains almost constant up to 70 min (curve D).

Measured against isoamyl alcohol the extracted brown tungsten(V) ferrocyanide complex has λ_{max} at 320 nm (Fig. 2, curve A) and no peak in the visible region even at higher tungsten concentrations

Table 3. Co-extraction of diverse elements and their effect on the extraction of tungsten(V) ferrocyanide*

Foreign species	Ammount (mg)	% Extraction of	
		Other element†	Tungsten§
—	—	—	99.0
Fe(III)	10	p	—
Fe(III)‡‖	10	0.6	86.0
Co(II)	10	p	—
Co(II)‡	10	0.4	70.85
Ni(II)	10	p	—
Ni(II)‡	10.	p	—
Mn(II)	1	0.0	95.55
Cr(VI)	10	p	—
Cr(VI)‡	10	0.2	85.2
V(V)	1	p	—
V(V)‡	1	p	—
As(V)	1	0.4	99.3
Sb(III)	1	1.72	99.1
Bi(III)	1	2.5	98.6
Si(IV)	10	1	98.7
Ca(II)	2	0.0¶	97.5
Cu(II)	2	0.6	70.5
Mo(VI)	1	p	—

* Tungsten 2 mg/25 ml (modified extraction procedure; except for Cr).
† Determined by conventional colorimetric methods;[4,10] p = precipitated.
§ By difference; tungsten determined in the aqueous phase by Hg–SCN method.[8]
‡ In presence of glycerol.
‖ Sulphosalicyclic acid added.
¶ By flame test, qualitatively.

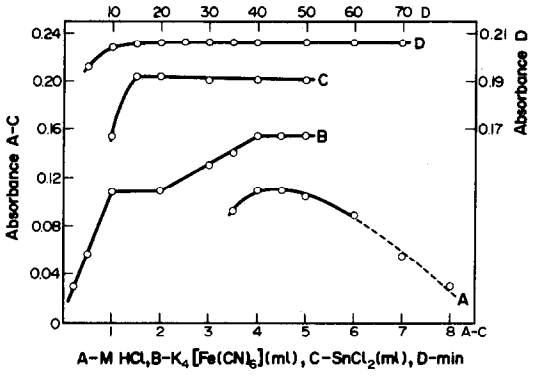

Fig. 1. Dependence of absorbance of tungsten(V) ferrocyanide in aqueous solution on various parameters (curves and corresponding scales on axes indicated by same letter). A–D W/4 μg/ml.

(1200 μg/25 ml, curve C). The reagent blank has λ_{max} at 311 nm with a shoulder at 330 nm, and no peak in the visible region (curve B).

Addition of tartaric acid and application of the procedure results in a broad asymmetric band with peak at 490 nm for tungsten > 200 μg/25 ml (Fig. 2, curves E–H). The sensitivity also increases (curves C and H). Therefore, this procedure is recommended for determination of tungsten. The absorbance is measured at 490 nm and Beer's law is obeyed up to 56 μg/ml (measurement against isoamyl alcohol). The sensitivity remains the same before and after the extraction with isoamyl alcohol, if measurements are made against reagent blanks similarly prepared. The blue colour formed by traces of iron impurity in the reagents may contribute slightly to the absorbance of the aqueous solution, but if an extraction with isoamyl alcohol is done the blue product appears as a scum at the interface and its effect can be avoided; therefore, extraction is recommended.

Tartaric acid, sodium chloride, sulphate and phosphate, even in large amounts, have little effect on the absorbance (Table 4) but acetate and oxalate decrease the absorbance and give turbidities and, on extraction, emulsions.

When present, iron, nickel, cobalt, chromium, molybdenum and copper are precipitated as their ferrocyanides, but cannot be dealt with by filtration as 25–40% of the tungsten is retained by the precipitate. Though glycerol can be used as masking agent (plus sulphosalicylic acid for iron), molybdenum is extracted and extraction of tungsten is decreased. A preliminary separation of molybdenum and nickel is necessary. The other elements can be dealt with by using the modified separation procedure given above.

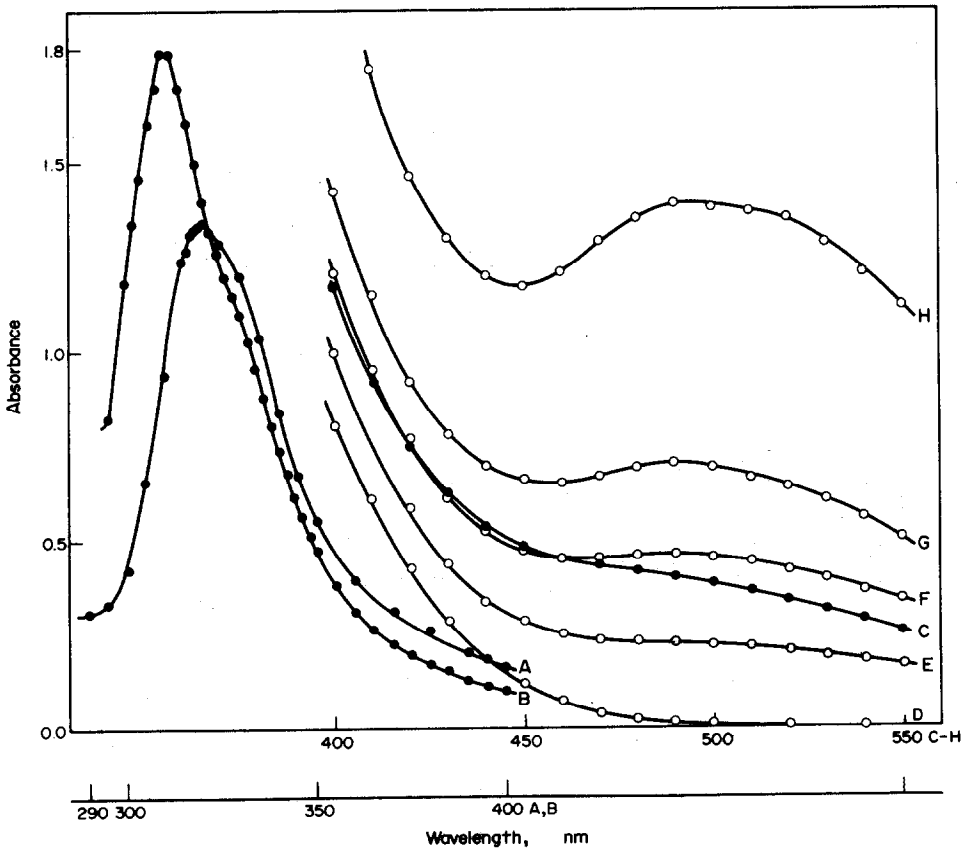

Fig. 2. Absorption spectra of tungsten(V) ferrocyanide complex in isoamyl alcohol. W, μg/ml: A 0.4, E 8, F 16, G 24, C and H 48; B and D, reagent blanks. A–C: by addition of all the reagents (tartaric acid absent). D–H: by the given spectrophotometric procedure.

Table 4. Effect of anions on the absorbance of tungsten(V) ferrocyanide in isoamyl alcohol (600 μg of tungsten in 25 ml)

Salt	Amount, *g/25 ml*	Absorbance (at 400 nm)
None	—	1.41
Sodium chloride*	1.0	1.39
Sodium sulphate*	1.0	1.35
Tartaric acid*	0.5	1.40
Trisodium phosphate*	1.0	1.40
Potassium acetate†	0.5	1.33§
Potassium oxalate†	0.5	1.24§

* Added before forming the complex.
† Added after forming the complex.
§ A turbidity remains in the aqueous phase, causing some emulsion which is filtered off.

Table 5. Analysis of samples by the proposed methods of separation and determination

Sample composition*		
Matrix, *mg*	W added, *mg*	W found, *mg*
Co(15), Cr(5)	5.0	5.02†,5.01
Fe(2.2), Mn(1.6), Sn(0.2), Bi(0.04), Ca(0.02)	10.0	10.0§,9.99
Fe(17), Ni(1.75), Cr(5), Mn(0.125)	1.0	1.00‡
Co(2.2), Cr(0.75)	2.0	1.99
Ferrotungsten A	75.2%	75.0% 75.3%,‡ 75.0%†
Ferrotungsten B	73.3%	73.1%, 73.4%,‡ 73.4%†
High-speed steel super rapid extra 500	18.0%	18.0%†

* Samples 1–4 are analogous to stellite, Spanish wolframite, Midvale HR and Haynes metal.
† Determination of tungsten by Hg–SCN method.[8]
§ Determination of tungsten as phosphotungsten blue.[9]
‡ Separation of tungsten by thiocyanate method.[11]

Applications

The extraction method separates tungsten from many important elements such as iron, cobalt, manganese, chromium, arsenic, antimony, bismuth, silicon, calcium and copper. Molybdenum, vanadium and nickel cannot be separated. Amounts of tungsten in the μg–mg range can be determined spectrophotometrically as the ferrocyanide complex itself after the separation. The methods are simple, use very common reagents and are generally applicable to many tungsten materials, both natural and industrial. The methods are shown to give satisfactory and reproducible results (Table 5) with an overall error of around 0.5% in various samples containing amounts of tungsten ranging from low to high.

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SHORT COMMUNICATIONS

SPECTROPHOTOMETRIC DETERMINATION OF TELLURIUM IN TRACE QUANTITIES BY USE OF AN ION-ASSOCIATION COMPLEX

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Summary—The formation of an ion-association complex by the interaction of iodotellurate(IV) with cetyltrimethylammonium bromide is used as the basis of an extractive procedure to determine tellurium in the range 2.5–12.5 μg in a final aqueous phase volume of 20 ml. The method is simple, reliable and sensitive. Selectivity is achieved by separation of tellurium on aluminium hydroxide as collector.

Relatively few spectrophotometric procedures are available for the routine determination of tellurium in different kinds of materials. Both the iodotellurate(IV) procedure reported by Johnson and Kwan[1] and the bismuthiol II method reported independently by Jankovsky and Ksir[2] and by Cheng[3] are quite sensitive, but they are restricted because under some conditions the reagents can undergo aerial oxidation to form products which absorb at the absorption maximum of the tellurium reagent complexes. The methods are also not particularly selective. Bode's diethyldithiocarbamate procedure[4] is highly selective under certain experimental conditions, but its sensitivity is very poor ($\epsilon = 3.2 \times 10^3$ l.mole^{-1}.cm^{-1}).

Efforts to extract the iodotellurate(IV) species selectively into organic solvents to increase its analytical utility have been reported in the literature.[5–8] A strongly acidic medium is used and hence there is extensive liberation of iodine by aerial oxidation of the iodide. These procedures are therefore more useful for separating tellurium from other elements[9] than for its determination.

The analytical application of ion-association interaction between iodotellurate(IV) and cationic surfactants has not been studied so far. Our work with such surfactants has indicated that cetyltrimethylammonium bromide (CTAB) is worth examining. This paper presents the details of the study.

EXPERIMENTAL

Reagents

Tellurium(IV) solution (2.5 ppm). Dissolve 0.050 g of metallic tellurium in 10 ml of concentrated nitric acid and boil carefully to remove nitrous fumes. Cool, transfer into a 500-ml standard flask and dilute to the mark to obtain a 100-ppm solution. Dilute this solution 40-fold.

CTAB solution (0.75%).

Potassium iodide solution (5%). Dissolve 12.5 g of potassium iodide and 5 g of sodium hypophosphite in water and dilute to 250 ml.

Procedure

Transfer a suitable portion of sample solution containing not more than 12 μg of tellurium into a 60-ml separating funnel. Add, with mixing, 2 ml of 5*N* sulphuric acid, 1 ml of CTAB solution and 2.5 ml of potassium iodide solution. Dilute to *ca.* 20 ml and shake for 2–3 min with 5 ml of chloroform. Drain the organic extract into a dry 10-ml volumetric flask containing a pinch of anhydrous sodium sulphate. Measure the absorbance of the extract at 360 nm in 5-mm cells against a reagent blank. Prepare a calibration graph covering the range 2.5–12.5 μg of tellurium by the above procedure.

RESULTS AND DISCUSSION

As the ion-association complex formed by iodotellurate(IV) and CTAB gradually precipitates, its extractability into organic solvents was examined. Chloroform seemed best. However, the results were found to be very erratic because of the liberation of iodine by aerial oxidation of iodide [the I_3^- thus formed reacts with CTAB similarly to iodotellurate(IV)]. Experiments conducted in the presence of reducing agents capable of suppressing iodine liberation indicated that hypophosphite is very effective [under these conditions, Te(IV) is not reduced]. Hence, hypophosphite was incorporated in the iodide reagent solution itself.

Absorption spectra

Figure 1 shows the absorption spectrum of the complex at different concentrations of tellurium. The complex has absorption peaks at 300 and 360 nm. Although the absorption at 300 nm is the higher, the blank values were also higher in this region and therefore the 360-nm peak was employed for analytical purposes.

Optimization of experimental conditions

Figure 2 shows the minimum concentration of iodide required for the formation of maximum amount of the ion-pair at various acidities. A final concentration of 0.5*N* sulphuric acid and 0.035*M*

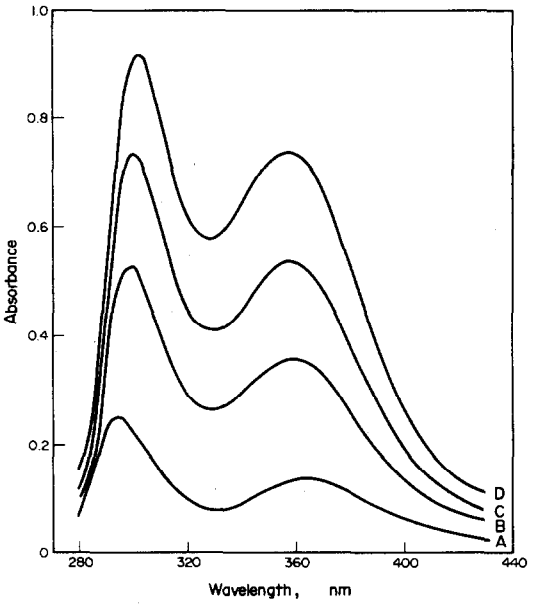

Fig. 1. Absorption spectra (A): 2 ml of 5*N* H_2SO_4, 2.5 ml of 5% KI–2% NaH_2PO_2 solution and 1 ml of 0.75% CTAB solution, diluted to 20 ml and extracted with 5 ml of $CHCl_3$. (B, C, D): as in (A) with the addition of 1 ml (B), 2 ml (C) and 3 ml (D) of 2.5 ppm Te(IV) solution.

potassium iodide was therefore chosen as optimal. A minimum of 2.5 ml of 0.15% CTAB solution was required to ensure maximum extraction of 10 μg of tellurium (Fig. 3). A higher concentration, *viz.* 1 ml of 0.75%, was employed in practice, as CTAB was found to help in suppression of aerial oxidation of iodide, for reasons not yet clarified.

It was also observed that hypophosphite does not affect the extraction. Shaking for 2 min was found sufficient to ensure maximum extraction of the ion-pair. The organic extracts were found to be stable for at least 90 min in daylight and for 25 hr in the dark. Slight variation in the final volume of aqueous phase did not affect the extraction significantly.

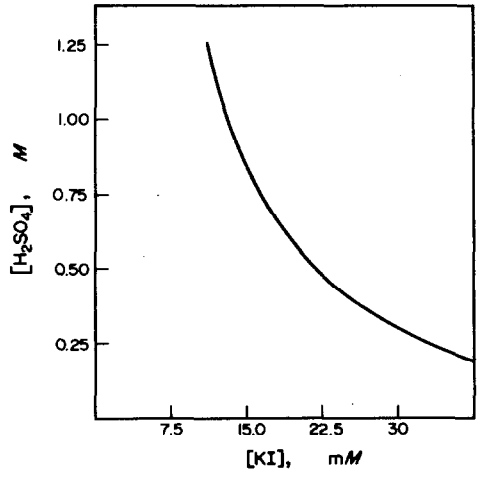

Fig. 2. Minimum KI concentration required for maximum extraction of the complex, as a function of acidity.

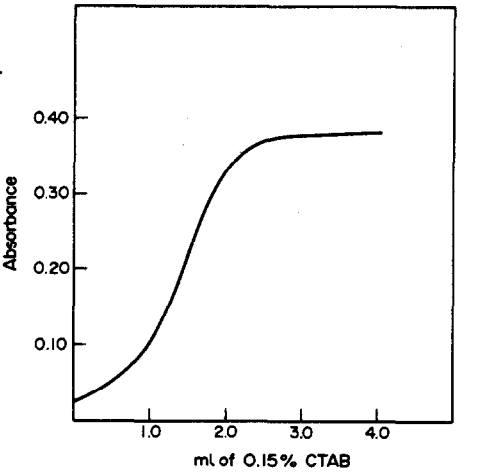

Fig. 3. Effect of CTAB concentration: 4 ml of 2.5 ppm Te(IV), 2 ml of 5*N* H_2SO_4, 0–4 ml of 0.15% CTAB solution and 2.5 ml of 5% KI–2% NaH_2PO_2, solution diluted to 20 ml and extracted with 5 ml of $CHCl_3$.

Beer's law and precision

Beer's law was applicable to the system in the range 0–12.5 μg of tellurium in a final aqueous phase volume of 20 ml. The molar absorptivity of the ion-pair was 4.9×10^4 l.mole^{-1}.cm^{-1}. For 28 determinations of 10 μg of tellurium, the relative standard deviation was 2%.

Interference studies

The influence of various ions on the determination of tellurium was examined, with 1 mg of ion along with 10 μg of tellurium. The results are presented in Table 1.

Separation of tellurium from the matrix by co-precipitation with aluminium hydroxide has been reported.[9] To deal with the interferents, a slightly modified version of this procedure was employed. Tellurium was selectively collected by adding 5 ml of a *ca.* 1% slurry of freshly precipitated aluminium hydroxide to the sample solution at pH 4–6 and containing 5 ml of 0.05*M* EDTA. The precipitate was dissolved in 2 ml of 5*N* sulphuric acid and the recommended procedure followed (the additional 2 ml of acid can be omitted but does no harm). It was thus separated from all the interfering ions listed in Table 1 except Fe(III), Se(IV), Sb(V) and V(V). The interference of Fe(III), Se(IV) and V(V) was eliminated by reduction with hydroxylammonium chloride in 2*N* sulphuric acid medium. The selenium formed was filtered off or extracted into chloroform before proceeding with the determination of tellurium. Sb(V) was reduced to Sb(III) with iodide and the Sb(III) masked with fluoride, the iodine liberated being extracted into chloroform before the addition of CTAB. Thus all the interferences encountered can be eliminated and no tellurium appears to be lost during the process.

Table 1. Interference studies

Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Be^{2+}, BO_3^{3-}, Al^{3+}, La^{3+}, Th^{4+}, Sn^{2+}, PO_4^{3-}, NO_3^-, Cr^{3+}, $S_2O_3^{2-}$, Mn^{2+}, F^-, ClO_4^-, Fe^{2+}, Co^{2+}, Ni^{2+}, oxalate, tartrate, citrate and EDTA	No interference
AsO_4^{3-}, NO_2^-, IO_3^-, SeO_3^{2-}, VO_3^-, $Cr_2O_7^{2-}$, Sb^{5+}, Fe^{3+}, Cu^{2+},	Interfere by oxidizing iodide to iodine
Ag^+, Tl^+, Pb^{2+}, Bi^{3+}	Interfere by precipitating as iodides
WO_4^{2-}	Interferes by precipitating as tungstic acid
MoO_4^{2-}	Reacts with CTAB to give a white precipitate
Cd^{2+}, Hg^{2+}, Sb^{3+}, Pd^{2+}, Pt^{4+}	Interfere by forming their iodo-complex–CTAB ion-association species; Cd^{2+} reduces the absorbance, while the rest enhance it

CONCLUSION

The method developed is an improved version of the iodotellurate(IV) method due to Johnson and Kwan. It is superior to the existing spectrophotometric methods in sensitivity, speed and flexibility of the experimental conditions and comparable to them in selectivity. Even though the iodotellurate(IV) system is used, aerial oxidation of iodide is suppressed by incorporating a reducing agent. Good selectivity is achieved by selective collection of tellurium on aluminium hydroxide.

During this study, it was established that the presence of CTAB is essential for the extraction of iodotellurate(IV) species, so the extracted complex must be an ion-association complex. Its composition could not be established by conventional methods because of the concomitant extraction of the cetyltrimethylammonium iodide ion pair, but this does not affect the analytical utility of the system.

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AMPEROMETRIC DETERMINATION OF SODIUM HYDROGEN SULPHITE WITH CHLORAMINE-T

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Summary—Amperometric titrations with chloramine-T at a rotating platinum electrode (RPE) and a dropping mercury electrode (DME) have been applied to the determination of sodium hydrogen sulphite over the concentration range 0.004–0.1*N*. With the RPE, the indirect titration is best, at pH between 3 and 6, whereas the DME can be used for either direct or indirect titrations, at pH around 7. Relative standard deviations of 0.5% were obtained by both methods, with relative errors not exceeding ±1%.

In previous studies on the polarographic behaviour of chloramine-T (CAT) at a dropping mercury electrode (DME)[1] and at a rotating platinum electrode (RPE),[2,3] we found that CAT underwent a two-electron reduction in the pH range 2–13, though the stability of the diffusion current was dependent on the characteristics of the electrode reaction at both electrodes. This report describes amperometric titrations with CAT, using the DME and the RPE, for the determination of sodium hydrogen sulphite, and compares the results.

The author and his co-workers[4] have reported that sodium hydrogen sulphite can be determined over the concentration range 0.01–0.1*N* by direct potentiometric titration with lead tetra-acetate in dilute acetic acid medium. However, this method could not be used for the determination of lower concentrations because of the volatility of sulphur dioxide. Although a considerable number of oxidizing reagents, including CAT, have been used for the titrimetric determination of hydrogen sulphite or sulphite,[5–7] these cannot be used successfully for direct titration in acidic solution, again because of the volatility of sulphur dioxide, and back-titration has been recommended.

In this study, therefore, the direct titration was performed in weakly acidic or neutral solutions in order to prevent the loss of sulphur dioxide. The possibility of extending the range of application of the method to relatively low concentrations has been investigated.

EXPERIMENTAL

Apparatus

A Yanagimoto Polarograph, Type PA-101, was used with the dropping mercury electrode (DME)[1] and rotating platinum electrode (RPE)[2,3] described earlier. The potentials are referred to an SCE connected to the solution through a potassium nitrate–agar salt bridge.

Reagents

Stock solution of chloramine-T (*CAT*), 0.05*M* (0.1*N*). Prepared as described.

Stock solution of sodium hydrogen sulphite, 0.05*M* (0.1*N*). Prepared fresh each day with air-free distilled water, and standardized by iodimetric titration.[6] The solution, stored under nitrogen at 25°, was found to decrease in normality by about 0.3% in 9 hr. Lower concentrations were prepared by appropriate dilution with air-free water. The pH was adjusted to about 7 to prevent loss of sulphur dioxide.

Other solutions such as potassium nitrate and Britton–Robinson buffer were prepared as reported earlier.[1,2] All solutions were prepared with doubly distilled water.

Procedure

Method A (*reverse titration*). Supporting electrolyte, (50 ml, 0.1*M* in potassium nitrate and containing a suitable buffer) and standard CAT solution (5.00 ml) of appropriate concentration were added to the cell and deoxygenated completely by passage of nitrogen. This solution was titrated with sodium hydrogen sulphite solution. After each addition of titrant, the solution was mixed by passage of nitrogen for 60–90 sec, and then the current was recorded. The measured currents were corrected for dilution. In order to prevent aerial oxidation of hydrogen sulphite, nitrogen was passed over the surface of the hydrogen sulphite solution in the burette during the titration. For titrations with the DME, 0.01% polyacrylamide (PAA) was added as a maximum suppressor.

Method B (*direct titration*). After 50 ml of the supporting electrolyte had been deoxygenated in the cell, 5.00 ml of the sodium hydrogen sulphite solution were added. The solution was titrated with standard CAT solution. In order to prevent induced aerial oxidation of hydrogen sulphite, the CAT solution was deoxygenated and stored under nitrogen in the burette during the titration. Other details were as for method A.

RESULTS AND DISCUSSION

Amperometric titration at a rotating platinum electrode (RPE)

The results of titrations by methods A and B for concentrations of around 0.01*N* in the pH range 3–7 are given in Table 1. All titrations except those at pH 7 were carried out at 0 V *vs.* SCE, while a potential of −0.5 V was applied to the indicator electrode

Table 1. Effect of pH on the amperometric titration at the RPE

pH	$[NaHSO_3]$ N	[CAT] N	End-point Calc., *ml*	End-point Found,* *ml*	Average error, %
Method A					
3.13	1.037×10^{-2}	0.984×10^{-2}	4.74	4.73 ± 0.02	−0.2
4.45	1.075×10^{-2}	0.984×10^{-2}	4.58	4.59 ± 0.02	+0.2
5.05	1.090×10^{-2}	0.984×10^{-2}	4.51	4.52 ± 0.02	+0.2
6.18	1.091×10^{-2}	0.984×10^{-2}	4.51	4.53 ± 0.02	+0.4
5.25†	1.060×10^{-2}	0.984×10^{-2}	4.64	4.67 ± 0.01	+0.6
Method B					
3.55	1.063×10^{-2}	0.973×10^{-2}	5.46	5.21 ± 0.01	−4.7
5.14	1.063×10^{-2}	0.973×10^{-2}	5.46	5.39 ± 0.02	−1.3
6.18	1.063×10^{-2}	0.973×10^{-2}	5.46	5.43 ± 0.01	−0.6
7.30†	1.010×10^{-2}	0.944×10^{-2}	5.35	5.34 ± 0.02	−0.2

* Average of 3 titrations.
† A potential of −0.5 V *vs.* SCE was applied.

for titrations at pH 7, because the chloramine-T reduction wave is shifted to more negative potentials as the pH rises. Titration curves of a normal L-shape and a reversed L-shape were obtained by methods A and B, respectively, because hydrogen sulphite showed neither a cathodic nor an anodic wave at the potentials applied over the pH range used.

Over the pH range 3–6, method A gives good results, but method B gives poor results, being worse at lower pH and also when the flow of nitrogen through the solution is increased, indicating that sulphur dioxide is being swept out of the solution under these conditions.

At pH 7, both methods are satisfactory for concentrations of 0.01*N*, indicating that sulphur dioxide is not lost at this pH. However, for higher concentrations the reduction current for the CAT became increasingly unstable and the titration plot became curved after the end-point, causing difficulty in extrapolation. This instability of the current is considered to be due to a deactivation effect[3] from some constituents adsorbed on the electrode surface. We can conclude that the titration at pH 7 cannot be successfully followed with the RPE.

From these results, it would seem that indirect titration (method A) with the RPE is best done at pH 5. Different concentrations within the range 0.001–0.1*N* were titrated under these conditions: the results are given in Table 2. Over the range 0.004–0.1*N* the relative errors did not exceed ±1.0%, and the coefficient of variation for 6 titrations was 0.5%. It was also found that the results were not affected by the presence of chloride, sulphate or *p*-toluenesulphonamide, which are the reaction products, at concentrations up to at least twice those produced in the titration reaction.

At concentrations below 0.002*N* the error became increasingly positive (Table 1); this is considered to arise from aerial oxidation of hydrogen sulphite during the preparation and storage of its solutions at concentrations around 0.001*N*.

Amperometric titration at a dropping mercury electrode (DME)

The results of titrations by both methods in the pH range 5–7 are given in Table 3. A potential of −0.2 V was applied, because an anodic wave appeared at around 0 V for the hydrogen sulphite

Table 2. Results obtained by the indirect amperometric titration with the RPE (method A) at pH 5.05

$[NaHSO_3]$ N	[CAT] N	End-point Calc. *ml*	End-point Found *ml*	Average error, %
1.025×10^{-1}	0.984×10^{-1}	4.80	4.81 ± 0.04*	−0.2
5.01×10^{-2}	4.93×10^{-2}	4.92	4.93 ± 0.02	+0.2
1.113×10^{-2}	0.951×10^{-2}	4.27	4.27 ± 0.01†	±0.0
8.89×10^{-3}	7.62×10^{-3}	4.29	4.30 ± 0.01	+0.2
5.11×10^{-3}	4.94×10^{-3}	4.83	4.83 ± 0.02	+0.2
4.37×10^{-3}	3.820×10^{-3}	4.37	4.40 ± 0.02	+0.7
2.284×10^{-3}	1.946×10^{-3}	4.26	4.36 ± 0.04	+2.3

* $s = 2.5 \times 10^{-2}$ ml (6 titrations).
† $s = 2.0 \times 10^{-2}$ ml (6 titrations).

Table 3. Effect of pH on the amperometric titration at the DME

pH	$[NaHSO_3]$ *N*	[CAT] *N*	End-point Calc. *ml*	End-point Found* *ml*	End-point Average error, %
Method A					
5.02	1.098×10^{-2}	0.991×10^{-2}	4.51	4.45 ± 0.02	−1.3
6.18	1.098×10^{-2}	0.991×10^{-2}	4.51	4.48 ± 0.01	−0.9
7.22	1.019×10^{-2}	1.001×10^{-2}	4.51	4.52 ± 0.02	+0.1
Method B					
7.30	1.010×10^{-2}	0.944×10^{-2}	5.35	5.33 ± 0.03	−0.4

* Average of 3 titrations.

solutions, as reported previously.[8] The titration curves obtained had the same shape as those obtained with the RPE.

Indirect titrations (DME, method A) at pH < 6, gave low results with the error increasing as the pH decreased, in contrast to the good results obtained when the RPE was used. The errors also increased with increasing nitrogen flow-rate, suggesting that the negative errors could be attributed to reaction between CAT and the pool of mercury.[1] The direct titration (method B) using the DME at pH < 6 gave low results similar to those obtained with the RPE. It is concluded that titrations using the DME should not be done at pH < 6.

On the other hand, the titrations by both methods with the DME at pH 7 gave good results. For the determination of sodium hydrogen sulphite over the concentration range of 0.004–0.1*N*, the relative errors did not exceed ±1.0% and the coefficient of variation of 6 titrations was 0.5%. The optimum conditions as found experimentally are in agreement with the facts that the diffusion current for CAT at the DME is very stable in neutral solutions, but not in acidic solutions, and that loss of sulphur dioxide from neutral solutions cannot be detected. The presence of added amounts of chloride, sulphate or *p*-toluenesulphonamide, did not affect the performance of this method.

CONCLUSIONS

Chloramine-T has been found to react quickly and quantitatively with hydrogen sulphite in neutral or weakly acidic solutions according to the equation

$$RSO_2NClH + HSO_3^- + OH^- \rightarrow RSO_2NH_2 + HSO_4^- + Cl^-$$

where $R = CH_3C_6H_4$. Based on this reaction, sodium hydrogen sulphite can be titrated directly with CAT over the concentration range 0.004–0.1*N* with amperometric end-point indication by means of either an RPE or a DME. When the RPE is used, good results can be obtained when CAT is titrated in weakly acidic solution with sodium hydrogen sulphite solution at 0 V *vs.* SCE. When the DME is used, good results can be obtained when CAT is titrated in neutral solution with sodium hydrogen sulphite solution, or *vice versa*, at −0.2 V *vs.* SCE.

It can be concluded that, for the standardization of sodium hydrogen sulphite solutions over the range 0.004–0.1*N*, the proposed amperometric methods with CAT are simpler and more accurate than previous methods, because the titrations are carried out under conditions where sulphur dioxide is not lost as gas from the solution.

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AMMONIUM 2-(2′-LEPIDYLAZO)-1-NAPHTHOL-4-SULPHONATE AS INDICATOR IN MERCURIMETRIC DETERMINATION OF HALIDES

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Summary—The use of ammonium 2-(2′-lepidylazo)-1-naphthol-4-sulphonate as indicator in titrimetric estimation of chloride, bromide and iodide with mercury(II) has been examined. The precision, accuracy and applicability of the procedures have been evaluated.

Sodium nitroprusside has been used as indicator[1–4] in mercurimetric determination of chloride ions. Other commonly employed indicators are diphenylcarbazide,[5,6] azo-derivatives of 8-hydroxyquinoline[7] and PAN.[8] For bromide estimation Trtílek[9] and McCleary[10] both consider the mercurimetric methods to be the more reliable. Various complexes have been proposed as indicators for titrimetric estimation of iodide.[11–14]

We now recommend ammonium 2-(2′-lepidylazo)-1-naphthol-4-sulphonate as indicator for mercurimetric estimation of halides in aqueous 2-propanol or dimethylformamide (DMF) medium.

EXPERIMENTAL

Reagents

Standard mercury(II) solution. Prepared by dissolving the metal in perchloric acid, evaporating nearly to dryness, adding more perchloric acid and evaporating again, this being repeated, and finally diluting to volume with water.

Halide solutions. Prepared by dissolving the requisite quantity of the potassium salt in doubly distilled water.

Buffer. Hexamine solution (10%).

Indicator. The salt was synthesized[15] and a 0.01% solution prepared in doubly distilled water.

Procedure

To a solution containing 0.07–35 mg of chloride, or 0.08–16 mg of bromide or 0.13–13 mg of iodide add 2 drops of indicator solution. Add 2–3 ml of hexamine–nitric acid buffer of pH 6.0–7.5 and, for chloride, enough 2-propanol to give a final concentration of 60–80%, or, for bromide and iodide, enough dimethylformamide to give a concentration of 0.5–2.5%. More is without effect, but less causes inaccurate results. Dilute to 20 ml and titrate with mercury(II) solution till the colour changes from light orange or yellow to blue. The relative error is generally 0.1–0.8%.

RESULTS

Effect of diverse ions

Cations which give colour reactions with LANAS [Pb, Cu, Co, Fe(II), Ni, Mn(II) Sc, Bi, Ga, lanthanides] under the titration conditions will interfere. Sulphate (2000 ppm), sulphite (1000 ppm), oxalate and phosphate (120 ppm), citrate (2500 ppm), tartrate (500 ppm), nitrite (200 ppm), nitrate and acetate (5000 ppm), barium, calcium, strontium and magnesium (500 ppm) and aluminium (30 ppm) are tolerated. Anions such as thiosulphate, cyanide and thiocyanate interfere, and so does thiourea.

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DETERMINATION OF NEPTUNIUM BY REDOX TITRATION

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Summary—A simple and quick method for the potentiometric determination of neptunium on the 2–5 mg scale has been developed. It consists of oxidation to Np(VI) by AgO or fuming with $HClO_4$, destruction of excess of AgO by sulphamic acid, reduction of Np(VI) to Np(IV) with a slight excess of standard Fe(II) in 2*M* H_2SO_4 and potentiometric titration of the excess of Fe(II) with standard Ce(IV). The precision is ±0.5%.

Relatively little attention has been paid to redox methods for the determination of neptunium. The only potentiometric method reported[1] gives good precision for 10–100 mg of neptunium but is limited to samples containing only Np(V), preferably in perchloric acid. Studies were therefore initiated in this laboratory to develop alternative redox methods for the determination of neptunium present in any redox state. This paper describes a redox method for use on the 2–5 mg scale.

EXPERIMENTAL

Reagents

Standard potassium dichromate solution. Made by dissolving a known weight of pure potassium dichromate (dried at 120°) in a known weight of water.

Ferrous ammonium sulphate solution (~0.2*M*). Prepared in 2*M* sulphuric acid and deaerated by passage of nitrogen.

Ceric sulphate solution (~0.05*M*). Prepared in 3M sulphuric acid.

Neptunium stock solution. Neptunium obtained from the Radiochemical Centre, Amersham, was purified by anion-exchange from nitric acid medium and used for preparation of a stock solution in ~2*M* nitric acid. The radiochemical purity was checked from the α-spectrum obtained with a silicon surface-barrier detector. Neptunium(IV) stock solution in 2*M* sulphuric acid was prepared by reducing the neptunium stock solution by adding ~0.1*M* hydrazine and heating on a water-bath for about an hour. The Np(IV) thus formed was extracted with 0.5*M* thenoyltrifluoroacetone in xylene and stripped into 2*M* sulphuric acid.

Sulphamic acid solution, 15%.

Apparatus

Weight burettes were prepared from polythene vials (~15 ml capacity) by drawing out the necks over a flame to give fine jets.

Procedure

A weighed fraction (containing 2–5 mg of neptunium) of the stock solution in nitric acid was taken in a cylindrical 50-ml glass titration vessel and silver (II) oxide (15–20 mg) was added to oxidize the neptunium to Np(VI); a clear black–brown solution was obtained. Then 1 ml of 15% sulphamic acid solution was added to destroy the excess of oxidant and a clear pink Np(VI) solution was obtained. After 5 min the Np(VI) was reduced to Np(IV) by addition of a weighed excess of standard ferrous sulphate solution and the solution was diluted to about 10 ml with 2*M* sulphuric acid. The excess of iron(II) was then titrated potentiometrically with standard ceric sulphate solution to the first end-point (normally at 600–800 mV), the end-point being determined as described by Drummond and Grant.[4]

In a few cases the final titration was done with ferroin as indicator.

In some experiments the neptunium was oxidized to Np(VI) by fuming with perchloric acid.[2]

The ferrous solution was standardized on the same day by potentiometric titration with standard dichromate solution and used to standardize the ceric sulphate solution; the polythene weight-burettes were used, and to achieve better accuracy, the final amounts of titrant were added as more dilute solutions (from weight burettes).

The amount of neptunium was calculated from

$$\text{Np} = 118.5\ (W_{\text{Fe(II)}} \times C_{\text{Fe(II)}} - W_{\text{Ce(IV)}} \times C_{\text{Ce(IV)}})\ \text{mg}$$

where

$W_{\text{Fe(II)}}$ = g of iron(II) solution added,
$W_{\text{Ce(IV)}}$ = g of ceric sulphate solution used,
$C_{\text{Fe(II)}}$ = concentration of iron(II) solution (meq/g), and
$C_{\text{Ce(IV)}}$ = concentration of ceric sulphate solution (meq/g).

RESULTS AND DISCUSSION

The work was aimed at developing a potentiometric method for neptunium determination, similar

Table 1. The effect of Np(IV) on potentiometric determination of Fe(II) by Ce(IV) titration

Approximate amount of Np(IV) added, *mg*	Fe(II) sulphate solution taken, *mg*	Ce(IV) sulphate solution required, *mg*	Ce(IV) solution equivalent to 100 mg of Fe(II) solution, *mg*
—	187.3	784.0	418.7
—	200.1	837.4	418.4
—	96.3	402.3	418.0
1.4	148.7	622.9	419.1
1.4	154.3	645.6	418.5
1.4	106.0	443.5	418.6
1.4	131.7	552.0	419.3
1.4	118.0	493.6	418.5

Table 2. Potentiometric determination of neptunium

No.	Np solution taken,* g	Fe(II) sulphate solution added, mg	Ce(IV) sulphate solution required,† mg	Np found, mg	Conc. of Np in the solution, mg/g
1	0.3746	186.1	295.6	2.439	6.51
2	0.6673	343.6	578.8	4.352	6.52
3	0.7238	378.9	654.8	4.724	6.52
4	0.4469	257.4	473.1	3.080	6.60
5	0.6520	338.1	572.6	4.267	6.54
6	0.4840	293.0	609.6	3.151	6.51
7	0.5222	256.5	392.8	3.410	6.53
8	0.5653	322.0	621.3	3.688	6.53
9	0.8573	479.7	911.1	5.561	6.49
					Mean 6.53 ± 0.03 Coulometric value = 6.480 ± 0.001

* Samples 6–9 were analysed 1½ months after the others, each batch being done in one day.
† Correction factor applied to convert weight of dilute solution into equivalent weight of more concentrated solution.

to the one used for plutonium,[3–5] by oxidation to Np(VI), quantitative reduction to Np(IV) with excess of ferrous solution, and back-titration of the excess with ceric sulphate.

The oxidation with silver(II) oxide or perchloric acid was shown to be quantitative by spectrophotometry. The oxidized solution showed no absorption at 960 and 980 nm [the wavelength of the characteristic absorption peaks for Np(IV) and Np(V) respectively].

From the standard redox potentials for the Np(VI)/Np(V) couple (1.14 V) and the Fe(III)/Fe(II) couple (0.77 V), it can be inferred that Fe(II) should reduce Np(VI) to Np(V), but as the potential of the Np(V)/Np(IV) couple is 0.74 V, Np(V) is unlikely to be reduced to Np(IV) by Fe(II) in dilute perchloric acid. However, addition of sulphate medium, which complexes with Np(IV) more strongly than with Np(V) shifts the potential of the Np(V)/Np(IV) couple sufficiently to make this reduction feasible and quantitative [the potential for the Np(V)/Np(IV) couple in 1*M* sulphuric acid is reported[6] to be 0.99 V]. In preliminary work the reduction of Np(VI) to Np(IV) with a small excess of ferrous sulphate in 1, 2 and

Table 3. Potentiometric determination of neptunium [oxidation to Np(VI) by fuming with $HClO_4$]

Np solution taken, g	Fe(II) sulphate solution added, mg	Ce(IV) sulphate solution required,* mg	Np found, mg	Conc. of Np in the solution, mg/g
0.6725	326.6	472.7	4.260	6.33
0.7469	298.9	242.8	4.783	6.40
0.7620	297.3	207.7	4.914	6.45
0.9191	353.9	233.8	5.913	6.43
0.7496	312.7	304.3	4.770	6.36
				Mean: 6.40 ± 0.05 Coulometric value = 6.32 ± 0.012

* See second footnote to Table 2.

Table 4. Neptunium determination with ferroin as visual indicator

Np solution taken, g	Fe(II) sulphate solution added, mg	Ce(IV) sulphate solution required,* mg	Np found, mg	Conc. of Np in the solution, mg/g
0.4295	279.4	569.0	2.899	6.75
0.6173	345.4	578.0	4.172	6.76
0.3899	422.1	1226.1	2.664	6.83
0.3521	431.3	1314.0	2.433	6.91
0.4405	365.7	906.4	3.038	6.90
0.8609	777.2	2068.2	5.793	6.73
				Mean: 6.81 ± 0.08 Potentiometric value = 6.79 ± 0.004

* See second footnote to Table 2.

5*M* sulphuric acid was examined by spectrophotometry and found to be quantitative in all three media; the 2*M* medium was chosen.

It is known that Np(IV) is oxidized by Ce(IV) in 1*M* sulphuric acid,[7] but from the difference in the formal potentials of the Np(V)/Np(IV) (0.99 V) and Fe(III)/Fe(II) (0.69 V)[8] couples in 1*M* sulphuric acid, a mixture containing Np(IV) and Fe(II) should give two end-points when titrated potentiometrically with Ce(IV), the first corresponding to the oxidation of Fe(II). This assumption was tested experimentally by titration of Fe(II) with Ce(IV) in the absence and presence of Np(IV). The results in Table 1 show that not more than 0.1% of the Np(IV) is oxidized during the titration of the Fe(II).

The results of replicate analyses by different methods are summarized in Table 2. It is seen that a precision of $\pm 0.5\%$ is achieved by using the silver(II) procedure and that the perchloric acid oxidation gives slightly poorer results. The results obtained by potentiometry agreed with those obtained by coulometry within 1% or less.

The precision achieved by the visual indicator method was only about $\pm 1\%$ and the values agreed within 1% with those obtained potentiometrically.

Uranium(VI) (up to ~200 mg) did not interfere. Drummond and Grant[4] made an extensive study of interferences in their method for potentiometric determination of plutonium, and as our method is very similar, the substances which do not interfere should be the same. Plutonium will interfere, of course.

The method is simple and rapid, suitable for determination of 2–5 mg of Np with a precision of $\pm 0.5\%$.

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USE OF COMPLEXING LIGANDS IN THE DETERMINATION OF ANTIMONY AND TIN BY ATOMIC-ABSORPTION SPECTROMETRY

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Summary—The atomic-absorption spectrophotometric determination of antimony is best achieved in the presence of either an ammonium fluoride, hydrochloric acid, nitric acid mixture, or one of the following complexing agents: tartaric acid, citric acid, oxalic acid, 2-mercaptopropanoic acid. The interference of the 29 metals tested is least in the ammonium fluoride–hydrochloric acid–nitric acid mixture and is similar in tartaric acid, citric acid and 2-mercaptopropanoic acid media. However, the interference is pronounced in oxalic acid. Tin can be determined if any of the complexing agents or 6*M* hydrochloric acid is present.

Atomic-absorption spectrophotometry (AAS) has been successfully used to determine trace amounts of antimony and tin.[1] The flames used are hydrogen–air, argon–hydrogen, air–acetylene and nitrous oxide–acetylene. The sensitivity for antimony or tin is greatly enhanced if stibine[2,3] or stannane[3] is generated and introduced into the argon–hydrogen flame. However, this method suffers from the disadvantage of requiring a separate apparatus for generation of the volatile hydrides. Furthermore, the most commonly used atomization flames for antimony and tin are air–acetylene and nitrous oxide–acetylene.

The ready hydrolysis of antimony and tin to form oxides has presented difficulties in the AAS determination of these metals in aqueous solution. The British Standard[4] for determining antimony and tin involves treatment of the sample with acetic acid and hydrogen peroxide. The precipitate is filtered off before addition of hydrochloric acid to dissolve antimony and tin. The prepared solutions of tin and antimony deteriorate with time and have to be prepared fresh for each analysis. Gouin, Holtz and Miller[5] have used a mixture of fluoroboric acid and nitric acid for dissolution of the sample, followed by addition of tartaric acid to ensure the retention of antimony in solution. However, antimony tartrate solutions slowly hydrolyse and must be prepared fresh.[7] Quarrell *et al.*[6] have used a mixture of fluoroboric acid and hydrogen peroxide to eliminate the interference of tin and lead in the determination of antimony, but the solution cannot be stored indefinitely without loss of antimony by hydrolysis.[7]

This paper reports the determination of tin and antimony by AAS in the nitrous oxide–acetylene and air–acetylene flames after dissolution of the samples in a hydrochloric acid–nitric acid mixture, and addition of ammonium fluoride, tartaric acid, oxalic acid, citric acid, or 2-mercaptopropanoic acid.

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EXPERIMENTAL

Apparatus

A Pye Unicam Model SP90 atomic-absorption spectrophotometer with an SP94 nitrous oxide attachment was used. The optimum instrumental conditions are shown in Table 1.

Reagents

Tartaric acid, ammonium fluoride, oxalic acid, citric acid, 2-mercaptopropanoic acid, nitric acid, hydrochloric acid, tin and antimony were of analytical grade or equivalent.

Procedure

Antimony(III) stock solutions (1000 ppm) were prepared by placing 1.000 g of the metal in each of five 500-ml conical flasks containing 30 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid. After the metal samples had dissolved, the solutions were treated with the complexing agents (one per flask, 10 g of ammonium fluoride, tartaric acid, citric acid or oxalic acid, and 30 ml of 2-mercaptopropanoic acid being used). The resultant solutions were transferred to 1000-ml flasks (plastic in the case of ammonium fluoride), and made up to the mark. The stock solutions for tin were prepared similarly. A sixth 1000 ppm stock tin solution was prepared containing 6*M*

Table 1. Instrumental conditions for the determination of antimony and tin

Parameter	Antimony	Tin
Wavelength, *nm*	231.15	224.6
Slit-width, *mm*	0.15	0.12
Burner slot, *cm*		
air–acetylene	10	—
nitrous oxide–acetylene	—	5
Observation height, *cm*	0.7	1.5
Fuel flow-rate *l./min*		
acetylene	1.6	4.5
air	5	—
nitrous oxide	—	4.4
Lamp current, *mA*	12	6.5
Damping control	×2	×2

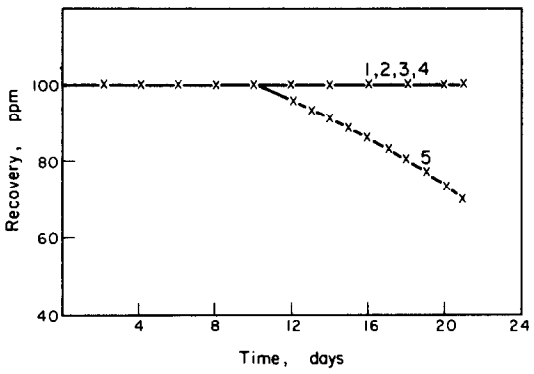

Fig. 1. Recovery of 100 ppm antimony(III) in the presence of 0.2% ammonium fluoride (1), oxalic acid (2), citric acid (3), tartaric acid (4) and 2-mercaptopropanoic acid (5) *vs.* time of storage.

hydrochloric acid only. Blank stock solutions of the complexing agents, containing 30 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid were prepared, together with one containing only 6*M* hydrochloric acid.

The calibration curves for Sb(III) in the various media were obtained by use of solutions containing 10, 20, 40, 60, 80, 100 and 120 ppm Sb(III). The concentration of complexing agent and mineral acid was kept constant by adding appropriate amounts of the appropriate blank solution. Similarly, the calibration curves for the tin solutions were obtained with 10, 40, 80, 120 and 200 ppm solutions.

The calibration curves for antimony were all linear up to 80 ppm Sb(III). The determination limit was about 0.5 ppm. The calibration curves for tin were all linear up to about 200 ppm. The determination limit was about 1 ppm.

The interference of other metals in the determination of antimony was tested by preparing solutions containing 50 ppm Sb(III) and 900 ppm of metals added as the following salts: $PdCl_2$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, K_2PtCl_6, NH_4VO_3, $FeCl_3.6H_2O$, $Pb(NO_3)_2$, $Al_2(SO_4)_3.16H_2O$, $BaCl_2.2H_2O$, $CaCl_2.2H_2O$, $CoCl_2.6H_2O$, $MgCl_2.6H_2O$, $MnCl_2.4H_2O$, $(NH_4)_6MoO_{24}.4H_2O$, LiCl, $LaCl_3.7H_2O$, KCl, $AgNO_3$, NaCl, $TiCl_4$, $(NH_4)_{10}W_{12}O_{41}.5H_2O$, $CdCl_2.2.5H_2O$, $SnCl_2.2H_2O$, $ZnSO_4.7H_2O$.

The hydrolysis of antimony and tin solutions in the presence of various complexing agents was studied by monitoring the absorbance of 100-ppm standard solutions over a period of three weeks. The results are presented in Fig. 1.

Table 2. Determination of antimony and tin in alloys

Complexing agent	Composition of alloy 1†		Composition of alloy 2§	
	Sb, %	Sn, %	Sb, %	Sn, %
NH_4F-HCl-HNO_3 mixture	12.0	74	12.4	80
citric acid	12.0	74	12.4	79
tartaric acid	12.0	75	12.5	79
2-mercaptopropanoic acid	12.1	74	12.5	81
Average composition, AAS*	12.0	74	12.4	80
Average composition, electron microprobe*	15.0	74	13.0	78

* Relative error ± 1%.

† Supplied by Generation Engineering (Th), Central Electricity Board, Mauritius (from U.K.). Other metals present Pb, 7.5%; Cu, 3.5%.

§ Supplied by Generation Engineering (Th), (from Italy). Other metals present Pb, 1.3%; Cu, 7.7%.

Two samples of alloys supplied by Generation Engineering (Th), Central Electricity Board, Mauritius (Sample 1 from U.K. and sample 2 from Italy), with antimony and tin as major constituents, were used to test the method. The two alloys were analysed by Butterworth Microanalytical Consultancy Ltd., England, for antimony and tin by the electron microprobe technique. The results are given in Table 2. The antimony solutions were analysed by using the air–acetylene flame, and the tin solutions with the nitrous oxide–acetylene flame.

RESULTS AND DISCUSSION

The chemistry of tervalent antimony in solution is dominated by its tendency to undergo hydrolysis to form insoluble hydroxides or oxides. Simple ionic species such as $Sb(H_2O)_x^{3+}$ do not exist in neutral or slightly acidic aqueous solution. Such hydrolysis could not be prevented in the blank stock solution containing 0.330*M* hydrochloric acid and 0.032*M* nitric acid. The formation of soluble antimonates with complexing ligands such as tartrate, fluoride, oxalate, citrate and 2-mercaptopropanoate occurs readily and minimizes the formation of hydrolysis products. The absorbance of 100-ppm Sb(III) solutions containing 0.2% of these complexing agents remained constant for three weeks (except for the 2-mercaptopropanoic acid solution which began to hydrolyse after 10 days).

The phenomenon of interference by other cations in the determination of an element by atomic-absorption spectrophotometry is well documented.[1] The interference of 29 metals at the 900-ppm level on the determination of antimony and tin has been studied. The effect on 50 ppm of antimony(III) in solutions containing various complexing agents and interfering ions may be summarized as follows.

When tartaric acid was the complexing agent the antimony value was correct within 2 ppm, except in the presence of platinum, magnesium, nickel, tin and tungsten, when it was low by 2–4 ppm.

When ammonium fluoride was used the antimony results were good (49–50 ppm) except in the presence of platinum, manganese and silver, where they were low by 2–3 ppm, and of nickel, when the value was high by 2 ppm.

When citric acid was used the results were correct in the presence of copper, calcium and sodium, but low by 1–2 ppm in the presence of the other metals.

When 2-mercaptopropanoic acid was used the results were correct in the presence of 10 of the metals tested and low by 1–10 ppm in the presence of the others.

Poorest results were obtained when oxalic acid was used as the complexing agent. The values were good (50 ppm) only in the presence of sodium, potassium and calcium. For all other interfering metals the values were low, 15 ppm for bismuth, 32 ppm for silver, 30 ppm for titanium, iron and lead, 35 for barium and 40–49 ppm for the remainder.

In a number of cases the added metal salts formed insoluble complexes with the ligands and the solutions had to be filtered before measurement. The con-

centration of antimony was reduced when such precipitates occurred because of co-precipitation or of hydrolysis resulting from a depleted concentration of ligand. The 2-mercaptopropanoic acid compounds could be dissolved by keeping the pH between 0 and 1. Examination of the results reveals that the ammonium fluoride, hydrochloric acid, nitric acid mixture gives the best and most consistent results throughout. The results for antimony in presence of tartaric, citric or 2-mercaptopropanoic acid are comparable but slightly lower than those obtained with ammonium fluoride. The results are lowest when oxalic acid is used as complexing agent, probably because of its inability to prevent hydrolysis at the pH of the solution.

The insoluble oxides of tin are normally redissolved by the addition of a minimum amount of 6*M* hydrochloric acid. It has been found that any of the five complexing agents can maintain tin in solution without hydrolysis. No decrease in absorbance was detected over a period of three weeks. Similarly, no decrease in absorbance for antimony(III) solutions was detected over a period of three weeks (except in the case of 2-mercaptopropanoic acid where a decreased absorbance reading was observed after 10 days as shown in Fig. 1).

Table 2 shows the results obtained for tin and antimony in two metal alloys, with use of the five complexing agents. The results are compared with those obtained by using an electron microprobe technique and it can be seen that the agreement is good.

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DIFFERENTIAL DETERMINATION OF TELLURIUM(IV) AND TELLURIUM(VI) WITH SODIUM DIETHYLDITHIOCARBAMATE, AMMONIUM PYRROLIDINEDITHIOCARBAMATE AND DITHIZONE BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY WITH A CARBON-TUBE ATOMIZER

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Summary—The extraction behaviour of tellurium(IV) and tellurium(VI) with sodium diethyldithiocarbamate, ammonium pyrrolidinedithiocarbamate and dithizone in organic solvents has been investigated by means of flameless atomic-absorption spectrophotometry with a carbon-tube atomizer. The selective extraction of tellurium(IV) and differential determination of tellurium(IV) and tellurium(VI) have been developed. With sodium diethyldithiocarbamate and carbon tetrachloride, when the aqueous phase/organic solvent volume-ratio is 5 and the injection volume in the carbon tube is 20 μl, the sensitivity for tellurium is 0.3 ng/ml for 1% absorption. The relative standard deviations are *ca.* 2%. The proposed methods have been applied satisfactorily to determination of tellurium(IV) and tellurium(VI) in various types of water.

Determination of tellurium in trace amounts has received increasing attention in connection with the wide application of its compounds and/or environmental pollution. Although tellurium is a comparatively rare element, it is widely used in the electronics industry. Occupational exposure to tellurium causes a sour garlic stench in the human breath.[1]

For determination of tellurium in various samples, atomic-absorption techniques based on the hydride[2] and a carbon-tube method[3,4] have been developed, and these methods enhance the sensitivity: they will not differentiate tellurium(IV) from tellurium(VI) however. In previous papers, differential determinations of arsenic(III) and (V),[5] antimony(III) and (V),[6] and selenium(IV) and (VI)[7] by solvent extraction combined with atomic-absorption spectrophotometry with a carbon-tube atomizer have been described. Recently, existing and potential solvent extraction methods for the separation of tellurium(IV) have been extensively reviewed by Havezov and Jordanov.[8]

In this paper, we extend to tellurium determination the techniques used for arsenic, antimony and selenium.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical-reagent grade chemicals and demineralized water, and stored in polyethylene bottles.

Standard tellurium(IV) solution, 1000 ppm. Prepared by dissolving 1.251 g of tellurium dioxide in 50 ml of 12*M* hydrochloric acid, and diluting to 1000 ml with water; further diluted with water to give a concentration of 1 ppm before use.

Standard tellurium(VI) solution, 1000 ppm. Prepared by dissolving 2.538 g of potassium tellurate ($K_2TeO_4 . 3H_2O$) and diluting to 1000 ml with water; further diluted with water to give a concentration of 1 ppm before use.

Buffer solution, pH 5.5. Prepared by mixing 1*M* acetic acid and 1*M* sodium acetate in a suitable ratio.

Apparatus

The apparatus was that described before,[5] except for the light-source, a Westinghouse tellurium hollow-cathode lamp.

Recommended general procedure

Tellurium(IV) determination. Take a fraction of sample solution, containing not more than 2 μg of tellurium(IV), in a separatory funnel. Add 5 ml of 5% EDTA solution. Add 2 ml of 2% sodium diethyldithiocarbamate (DDTC) solution and 5 ml of the acetate buffer solution. Dilute the mixture to 25 ml with water and shake the funnel for 2–5 min with 10.0 ml of carbon tetrachloride. Let stand for 20–30 min and separate the organic phase. Inject 20 μl of the organic phase by micropipette into the carbon tube. Pass argon through the furnace at a flow-rate of 3 l./min, and then atomize the sample by the following heating sequence: drying for 30 sec at 20 A (*ca.* 200°), ashing for 120 sec at 50 A (*ca.* 700°), and atomization for 7 sec at 230 A (*ca.* 2400°). Record the absorption signal at 214.3 nm. Run a reagent blank at the same instrumental settings and subtract it from the analytical value.

Total tellurium determination. Take an aliquot of sample solution containing not more than 2 μg of tellurium, in a beaker. Add hydrochloric acid to adjust the acidity of the solution to *ca.* 4*M*. Heat in a boiling water-bath or a steam-bath for 70 min. Cool, add 5 ml of 5% EDTA solution and 2 drops of Methyl Orange solution. Neutralize with ammonia solution. Add 2 ml of 2% DDTC solution and adjust the pH to 5–8 with 5 ml of the buffer

solution. Transfer the mixture to a separatory funnel and adjust the volume to 25 ml with washings from the beaker. Extract and measure the atomic absorption as for tellurium(IV). The tellurium(VI) is estimated from the difference between total tellurium and tellurium(IV).

RESULTS AND DISCUSSION

Optimization of the atomization system

The heating conditions were examined in the same way as for arsenic[5] and followed the same pattern, the useful limits being 20–30 A for 30 sec (200–300°) for drying, 45–55 A for 120 sec (650–800°) for ashing, and 190–250 A for 7 sec (2000–2600°) for the atomization.

The optimum shielding-gas flow-rate was 3 l./min.

Extraction

Extraction behaviour of Te(IV) and Te(VI). The extraction behaviour of tellurium(IV) and tellurium(VI) with DDTC, APDC (ammonium pyrrolidinedithiocarbamate) and dithizone in methyl isobutyl ketone (MIBK) and carbon tetrachloride was investigated. The effect of acidity is shown in Figs. 1–3.

In the DDTC system, tellurium(IV) is extracted into both carbon tetrachloride and MIBK in the pH range 3–9 whereas tellurium(VI) is not. In neutral medium, carbon tetrachloride gives much higher sensitivity and wider range of optimum pH than MIBK. The species extracted from neutral medium was confirmed to be $Te(DDTC)_4$ by continuous-variation plots. In concentrated hydrochloric acid medium, tellurium(IV) is extracted into MIBK, probably owing to the formation of chloro complexes. However, it is not extracted into carbon tetrachloride. The quite different behaviour of the two solvents, carbon tetrachloride and MIBK, seems very curious, but the cause was not discovered in this work. The apparently higher degree of extraction from concentrated (9*M*) hydrochloric acid medium (Fig. 1) probably results from the decrease in the volume of the organic phase because of the greater solubility of MIBK in such

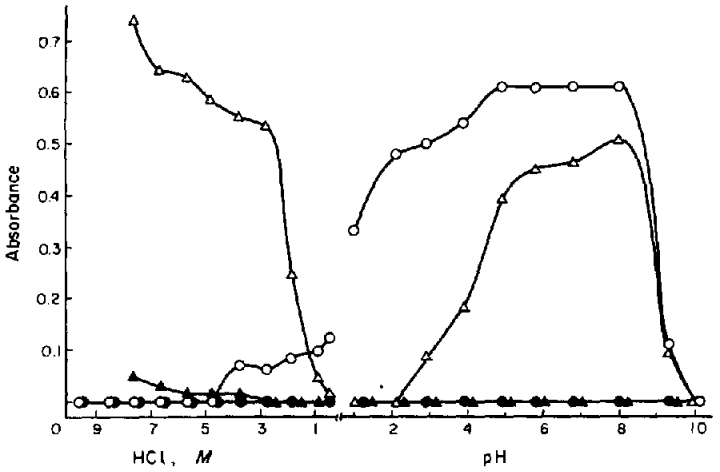

Fig. 1. Effect of acidity on the extraction of Te(IV) and Te(VI) with DDTC. ○, Te(IV)–CCl_4; ●, Te(VI)–CCl_4; △, Te(IV)–MIBK; ▲, Te(VI)–MIBK; aqueous phase, 25 ml; organic phase, 10 ml; Te(IV) or Te(VI), 2 μg.

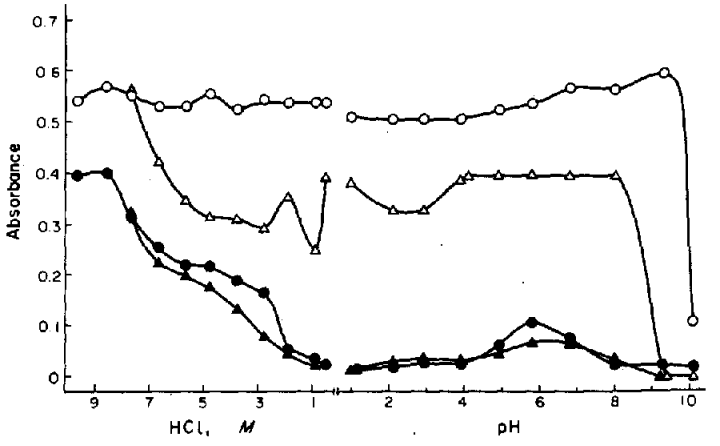

Fig. 2. Effect of acidity on the extraction of Te(IV) and Te(VI) with APDC. ○, Te(IV)–CCl_4; ●, Te(VI)–CCl_4; △, Te(IV)–MIBK; ▲, Te(VI)–MIBK; aqueous phase, 25 ml; organic phse, 10 ml; Te(IV) or Te(VI), 2 μg.

Table 1. Recovery tests on tellurium(IV) and tellurium(VI)

Added, *ng/ml*		Found, *ng/ml*		
Te(IV)	Te(VI)	Te(total)	Te(IV)	Te(VI)
0	80	77	0	77
20	60	76	20	56
40	40	79	40	39
60	20	77	60	17
80	0	80	80	0

a solution. Tellurium(VI) is not extracted from any medium.

With the APDC system, tellurium(IV) is extracted into both solvents over a wide range of pH. The sensitivity, however, is lower than that of the DDTC system. The degree of extraction of tellurium(VI) is much lower at pH 1–10 than that of tellurium(IV), but in strongly acidic medium both tellurium(IV) and (VI) are extracted.

Dithizone extracts tellurium(IV) very slightly from neutral medium into carbon tetrachloride or MIBK and from acidic medium into MIBK, but it does not extract tellurium(VI) from any medium.

Differential determination of Te(IV) and Te(VI). From the results it is concluded that extraction with DDTC into carbon tetrachloride at pH 5–8 is best for the selective separation of tellurium(IV) and (VI). Total tellurium is separately determined by extraction after reduction of tellurium(VI) to (IV). Recovery tests showed (Table 1) that the recommended procedure gave good results.

In the conventional method, tellurium(VI) is reduced to tellurium(IV) in warm hydrochloric acid. Temperature, time, and acid concentrations must be specified if quantitative reduction without loss of tellurium is to be obtained. The optimum conditions for the reduction were therefore investigated, by tests with 2 μg of tellurium(VI) in a boiling water-bath. Figure 4 shows that the heating time needed for the reduction in 4*M* hydrochloric acid is at least 60 min, and that there is no appreciable loss of tellurium after 80 min. The optimum acidity is 3.0*M* hydrochloric acid or above (Fig. 5).

Effect of shaking time, and stability of the extracts. Extraction is quantitative in 15 sec, and continued shaking for up to 20 min produces no further change in the atomic-absorption signal. The absorption of

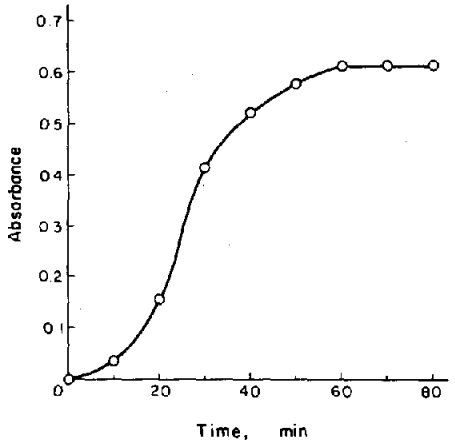

Fig. 4. Effect of heating time on reduction of Te(VI). Te(VI), 2 μg; hydrochloric acid, 4*M*; temperature, 100°C; aqueous phase 25 ml, organic phase 10 ml.

the extract remains almost constant for at least 5 hr after the extraction.

Effect of phase-volume ratio on sensitivity. To examine the effect of the volume ratio on the sensitivity of atomic absorption, 10 ml of carbon tetrachloride were used for the extraction from various volumes of the aqueous phase, each containing 2 μg of tellurium(IV). As the aqueous–organic phase volume-ratio (V_w/V_o: 1–10) was increased, the measured atomic absorption slightly decreased. If an appropriate V_w/V_o ratio is chosen according to the tellurium content of the samples, it is possible to determine tellurium over a wide range of concentration from ng/ml to μg/ml levels.

Calibration curve and precision

Calibration curves prepared by use of tellurium(IV) and reduced tellurium(VI) solutions were similar. The linearity was good over the range 2–40 ng/ml with $V_w/V_o = 5$. The sensitivity for 1% absorption was found to be 0.3 ng/ml. The relative standard deviation was *ca.* 2% for 80 ng/ml of tellurium(IV) (ten determinations, three injections in each).

Interferences

The interference of large amounts of alkali and alkaline earth metals in the determination of tellurium by direct injection is avoided by the prior extrac-

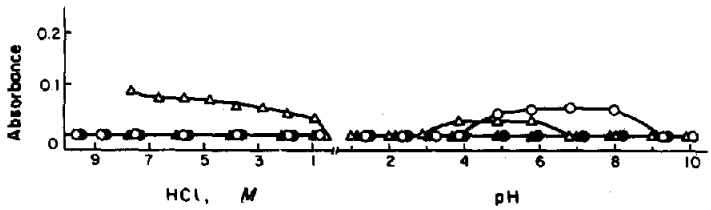

Fig. 3. Effect of acidity on the extraction of Te(IV) and Te(VI) with dithizone. ○, Te(IV)–CCl_4; ●, Te(VI)–CCl_4; △, Te(IV)–MIBK; ▲, Te(VI)–MIBK; aqueous phase, 25 ml; organic phase, 10 ml; Te(IV) or Te(VI), 2 μg.

Table 3. Analytical results on various samples

Sample	Te(total), *ng/ml*		Te(IV), *ng/ml*		Te(VI), *ng/ml*	
	added	found	added	found	added	found
River water A	—	ND	—	ND	—	ND
River water A	20	20	20	20	—	ND
River water A	20	18	—	ND	20	18
River water A	40	38	20	20	20	18
River water B	—	ND	—	ND	—	ND
River water B	20	20	20	20	—	ND
River water B	20	20	—	ND	20	20
River water B	40	40	20	20	20	20
Sea-water A	—	ND	—	ND	—	ND
Sea-water A	20	20	20	20	—	ND
Sea-water A	20	18	—	ND	20	18
Sea-water A	40	38	20	20	20	18
Sea-water B	—	ND	—	ND	—	ND
Sea-water B	20	20	20	20	—	ND
Sea-water B	20	18	—	ND	20	18
Sea-water B	40	38	20	20	20	18

ND: not detected.

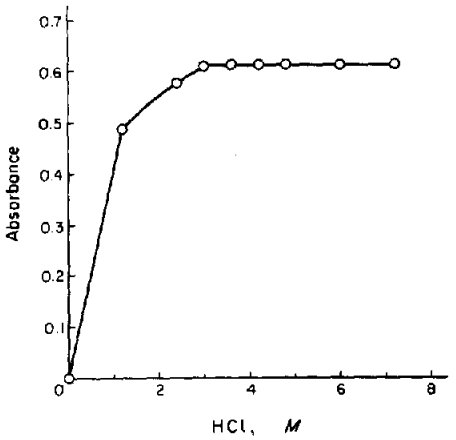

Fig. 5. Effect of hydrochloric acid concentration on reduction of Te(VI). Te(VI), 2 μg; temperature, 100°C; heating time, 70 min; aqueous phase 25 ml, organic phase 10 ml.

Table 2. Permissible amount of foreign ions in determination of 2 μg of Te/25 ml (with error $< -10\%$)

Ion	Added as	Limiting ratio, [ion]/[Te]
Fe^{3+}	Chloride	11
Ni^{2+}	Chloride	75
Cu^{2+}	Sulphate	1
Zn^{2+}	Chloride	130
Hg^{2+}	Chloride	37
Sn^{2+}	Sulphate	10
Cd^{2+}	Sulphate	5
Bi^{3+}	Chloride	5
Se(IV)	Selenious acid	3
As(III)	Arsenious acid	1
Sb(III)	Chloride	4

The following are tolerable in 1000-fold ratio to Te: Na^+, K^+, Ca^{2+}, Mg^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+}, Al^{3+}, Pb^{2+}, As(V), NH_4^+, F^-, Cl^-, Br^-, I^-, S^{2-}, NO_3^-, CH_3COO^-, SO_4^{2-}, PO_4^{3-}.

tion of the tellurium. However, large amounts of metal ions which react with DDTC lower the degree of extraction of tellurium(IV). Although such interferences can be reduced by masking with EDTA in many cases, iron(III), copper(II), cadmium(II), tin(II), *etc.* were found to interfere considerably with the determination of tellurium. Table 2 shows the effects of various ions; the data were obtained with 1% of EDTA in the aqueous phase.

Application to water analysis

Results for differential determination of tellurium(IV) and tellurium(VI) in various types of water are presented in Table 3 together with those of a recovery test on the samples. All the samples were acidified with hydrochloric acid to *ca.* pH 1 immediately after sampling. According to the method proposed here, ng/ml levels of tellurium(IV) and tellurium(VI) in waste water or sea-water can be determined satisfactorily.

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APPLICATIONS ANALYTIQUES DES OXOCARBONES—I

COMPOSITION ET CONSTANTES DE STABILITE DES COMPLEXES MOLYBDIQUES DE L'ION BROMANILATE: DOSAGE SPECTROPHOTOMETRIQUE DU MOLYBDENE(VI)

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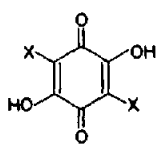
Résumé—L'ion bromanilate B^{2-} est un anion aromatique cyclique apparenté aux oxocarbones. Nous avons montré par spectrophotométrie ultraviolet–visible qu'il forme deux complexes 1:1 avec le molybdène(VI) en solution aqueuse à pH $\leqslant$ 6. Les variations de la constante conditionnelle de complexation avec l'acidité permettent de calculer le nombre de protons intervenant dans chaque équilibre. Les formules des deux complexes diffèrent d'un proton, le pK d'ionisation étant égal à 2,30. L'acide bromanilique H_2B permet de doser Mo(VI) à λ = 340 nm en milieu $HClO_4$ 3M ou 1,4M avec une précision meilleure qu'en utilisant l'acide chloranilique H_2C pour des concentrations voisines de 1 mg/l. Les meilleurs résultats obtenus avec H_2B quand l'acidité augmente ont été expliqués par l'écart entre les valeurs de pK_1 des deux acides: pK_1 = 0,22 pour H_2B et 0,45 pour H_2C.

En 1963, West[1] fut le premier à définir le concept d'"oxocarbones", composés comportant une chaîne de plusieurs atomes de carbones doublement liés aux atomes d'oxygène. Parmi ces corps, une série remarquable est formée par les anions cycliques dans lesquels plusieurs (deux en général) charges négatives sont délocalisées sur un nombre supérieur de groupements carbonyle. West[1] a calculé pour un grand nombre de ces oxocarbones l'énergie de délocalisation et montré que tous ces anions sont aromatiques.

L'un de nous a récemment[2] émis l'hypothèse que tous les anions **II** des dihydroxyquinones **I** appartenaient à la série des oxocarbones (quels que soient les substituants X) et non pas seulement, comme l'avait supposé West,[1] ceux porteurs de substituants déjà aromatiques tels que des groupements phényle. Nous avons entrepris, en conséquence, l'étude des propriétés des ions bromés et chlorés **IIa** et **IIb**.



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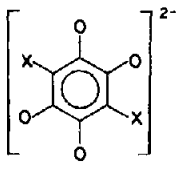


II

(a) X = Br acide bromanilique ion bromanilate
(b) X = Cl acide chloranilique ion chloranilate

Les études effectuées depuis plusieurs années au laboratoire nous ont permis de montrer que les oxocarbones présentent un ensemble de propriétés qui en font des réactifs analytiques d'un grand intérêt potentiel:

(1) solubilité notable dans l'eau,
(2) stabilité chimique vis-à-vis des acides et des bases,
(3) spectres (dans l'ultra-violet–visible) intenses, permettant d'exploiter avec précision les techniques spectrophotométriques,
(4) forte acidité des acides conjugués.

L'intérêt de ce dernier point est que les oxocarbones sont des bases faibles et ne sont masqués par les protons qu'en milieu très acide. En conséquence, l'emploi des oxocarbones semble particulièrement indiqué pour le dosage spectrophotométrique sélectif des éléments donnant des ions hydrolysés en milieu acide (pH voisin de zéro), d'autant plus que les cations métalliques ou alcalino-terreux forment en général des sels chélatés insolubles.[3,4]

Toutes ces caractéristiques expliquent le nombre considérable d'applications analytiques qu'a reçu l'ion chloranilate **IIb**. Nous avons d'ailleurs pris celui-ci comme premier exemple et précisé la nature de ses complexes molybdiques en solution et à l'état solide.[5]

Dans ce travail, nous avons examiné les propriétés complexantes de l'ion bromanilate **IIa** vis-à-vis des ions du molybdène(VI). Les deux acides **Ia** et **Ib** sont de force comparable. Cependant, les travaux antérieurs divergent quant à leurs sensibilités respect-

ives. **IIa** serait le réactif le plus sensible[6] pour le dosage du zirconium(IV) en milieu acide perchlorique 2,8*M*. Au contraire, les sels de baryum de **IIa** et **IIb**[7] ont des solubilités équivalentes en solution aqueuse neutre.

L'acide chloranilique ayant été utilisé[8] pour le dosage spectrophotométrique du molybdène(VI) en milieu acide perchlorique concentré, nous avons examiné le gain de sensibilité réalisé en le remplaçant par l'acide bromanilique. Les résultats ont été discutés à partir de la différence d'acidité des deux réactifs, que nous avons déterminée.

PARTIE EXPERIMENTALE

Appareils

On a utilisé un spectrophotomètre Unicam SP 800 B équipé de cuves en quartz Hellma de 10,00 et 1,00 mm d'épaisseur. Le compartiment des cuves était thermostaté à 298,0 ± 0,2 K par un cryostat Lauda K 2R.

Les valeurs de pH ont été mesurées avec un pH-mètre Metrohm E 353 B, équipé d'électrodes de verre combinées EA 120 X.

Réactifs

L'acide bromanilique était un produit Eastman et l'acide chloranilique un produit Fluka "puriss". Ils ont été utilisés sans purification. Le molybdate de sodium était un produit Prolabo pur. Tous les autres réactifs étaient des produits commerciaux "pour analyses".

Les solutions des réactifs étaient préparées par pesée et utilisées dans la semaine suivante.

Notations utilisées

L'acide bromanilique sera désigné par H_2B et ses ions par HB^- et B^{2-}. L'acide chloranilique et ses ions seront notés H_2C, HC^- et C^{2-}.

L'absorbance d'une solution a été notée A, le symbole ϵ représentant les absorbances molaires (en $l.mole^{-1}.cm^{-1}$).

La force ionique d'une solution a été notée I (en mole/l.).

La concentration analytique d'un corps X a été symbolisée par $[X]_T$.

La loi d'action de masse a été appliquée aux équilibres de complexation de façon à calculer des constantes de formation. En général, il s'agit de constantes conditionnelles de stabilité, que nous avons désignées par K_f. Nous nous sommes conformés à la terminologie de Ringbom.[9]

RESULTATS ET DISCUSSION

Constantes d'acidité de l'acide bromanilique

Les solutions d'acide bromanilique et de ses ions sont différemment colorées, ce qui permet de déterminer les valeurs de pK_a par spectrophotométrie dans le visible, où les différences entre les trois spectres sont importantes.

D'après la littérature,[10] les valeurs de pK_1 et pK_2 seraient respectivement de 0,80 et 3,10 (milieu non précisé). On peut donc prévoir que les deux ionisations ne sont pas indépendantes, et que la formation du monoion HB^- n'est jamais complète.

Or, la méthode colorimétrique exige la connaissance précise des absorbances des trois espèces. Celles de H_2B et de B^{2-} ont été obtenues respectivement en milieu $HClO_4$ 4*M* et en milieu de pH > 6. Nous avons calculé celle de HB^- dans la zone de pH > 3 (où le second équilibre d'ionisation intervient seul), par itérations successives, jusqu'à l'obtention d'une valeur constante de pK_2. L'absorbance molaire déterminée pour HB^- a ensuite été utilisée pour le calcul de pK_1 avec des résultats satisfaisants.

Le pK_1 étant faible, il n'est pas possible d'utiliser le pH pour définir l'activité des protons dans les mélanges H_2B–HB^-, la molarité $[H^+]$ étant supérieure à 0,1*M*. Aussi avons-nous utilisé la fonction d'acidité H_0 établie dans l'acide perchlorique par Yates et Wai.[11] Il n'est alors pas nécessaire de maintenir constante la force ionique des solutions.

Nos résultats sont, à 298 K:

$pK_1 = 0{,}22 \pm 0{,}05$ par rapport à H_0[11]
$pK_2 = 2{,}70 \pm 0{,}05$ ($I = 0{,}1M$)

On a opéré dans les conditions suivantes:

$$[H_2B]_T = 1{,}5.10^{-3}M$$

mesures effectuées à $\lambda = 530$ nm (cuves de 1 cm)

$$\epsilon_{H_2B} = 60\ l.mole^{-1}.cm^{-1}$$
$$\epsilon_{HB^-} = 853\ l.mole^{-1}.cm^{-1}\ \text{(calculé)}$$
$$\epsilon_{B^{2-}} = 187\ l.mole^{-1}.cm^{-1}$$

zone d'acidité pour la mesure de pK_1:

$$HClO_4\ 4{,}15M \text{ à } HClO_4\ 0{,}1M$$

Etude du système ion bromanilate–H^+–Mo(VI) en solution

La méthode suivie consiste à déterminer par spectrophotométrie la composition des complexes et leur constante conditionnelle de stabilité K_f à différents pH. La variation de K_f avec le pH donne le nombre de protons intervenant dans chaque équilibre.[9]

La modification du spectre dans le visible des espèces bromaniliques par complexation, bien que nette, est relativement peu intense pour une étude quantitative. C'est pourquoi les mesures ont été faites dans l'ultraviolet afin d'avoir une meilleure précision.

Composition des complexes. A toute acidité comprise entre $HClO_4$ 4*M* et pH 6, on a trouvé que les complexes se forment dans le rapport 1:1. Un exemple de la variation d'absorbance observée en fonction de l'addition de Mo(VI) à une solution de B^{2-} à pH 4,00 est donné en figure 1.

Zone $[HClO_4] > 1M$. Les réactifs se trouvent en milieu acide sous forme d'ions $HMoO_3^+$ et de molécules H_2B. Puisque le complexe est dissocié par acidification, on met en évidence l'équilibre de formation d'un complexe X, monomère:

$$HMoO_3^+ + H_2B \rightleftharpoons X + nH^+$$

En effet, seuls les coefficients stoechiométriques 1 et 1 permettent de calculer une valeur constante de K_f à chaque acidité. K est la constante apparente de

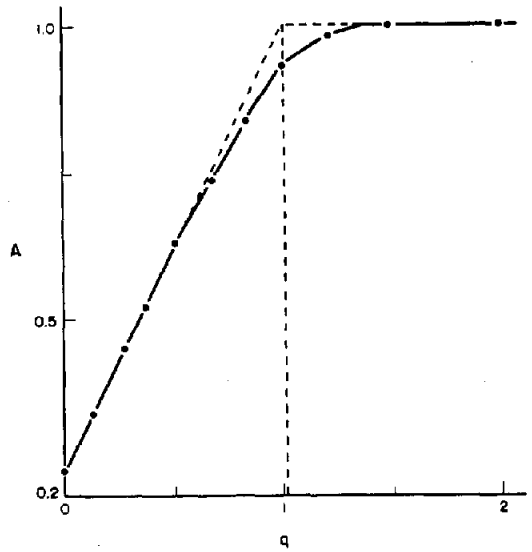


Fig. 1. Composition du complexe bromanilique de Mo(VI) à pH = 4,00.

$$[H_2B]_T = 5.10^{-4}M;\quad q = \frac{[Mo(VI)]_T}{[H_2B]_T};$$

l = 0,100 cm; λ = 350 nm; tampon acétique 0,2M.

l'équilibre ci-dessus. K_f doit varier avec $[H^+]$ selon $K_f = K[H^+]^{-n}$.

$$K_f = \frac{[X]}{[HMoO_3^+][H_2B]};\quad K = \frac{[X][H^+]^n}{[HMoO_3^+][H_2B]}$$

Nous avons calculé K_f à différentes concentrations en acide perchlorique. Afin de pouvoir raisonner sur la concentration des protons, nous avons imposé une force ionique élevée: 4M en ion perchlorate, ce qui fixe la valeur des coefficients d'activité. Les résultats sont exposés dans le tableau 1. K est une constante si l'on prend $n = 2$.

La dernière ligne du tableau 1 permet de montrer l'influence de la force ionique sur l'équilibre de complexation. Quand la molarité de $HClO_4$ est fixée à 1M, la proportion de complexe formé diminue par introduction de $NaClO_4$.

Le complexe se forme donc suivant l'équilibre:

$$HMoO_3^+ + H_2B \rightleftharpoons X + 2H^+$$

L'augmentation du nombre de particules par formation de X explique que l'accroissement de la force ionique défavorise la complexation, ce qui était inattendu.

Tampon acétique 0,2M. Entre pH 4 et pH 7, la proportion de complexe à l'équilibre diminue quand le pH augmente. Comme dans le cas du complexe chloranilique, on peut montrer[5] que l'espèce molybdique libre qui prédomine est MoO_4^{2-} dans les conditions retenues de concentration et de pH. En effet, l'ion $Mo_7O_{24}^{6-}$ est décondensé vers pH 4,50 par l'abaissement de la concentration de Mo(VI) libre due à la formation quantitative du complexe, et vers pH 5,50 par la diminution de $[H^+]$.

Tableau 1. Variation de la constante conditionnelle de complexation avec l'acidité perchlorique (I = 4,00M; T = 298 K)

$[HClO_4]$, M	$[NaClO_4]$, M	K_f	$K = K_f[H^+]^2$
2,00	2,00	$1,85.10^3$	$7,40.10^3$
1,00	3,00	$7,60.10^3$	$7,60.10^3$
0,50	3,50	$3,15.10^4$	$7,90.10^3$
1,00	0,00	$1,20.10^4$	—

L'équation de complexation doit donc s'écrire:

$$MoO_4^{2-} + B^{2-} + nH^+ \rightleftharpoons X'$$

Le complexe a été désigné par X', car son spectre est différent de celui de X, formé en milieu plus acide.

A chaque acidité, on calcule la constante conditionnelle K_f:

$$K_f = \frac{[X']}{[MoO_4^{2-}][B^{2-}]}$$

K_f est reliée à K, constante apparente de l'équilibre, et à $[H^+]$ par la relation $K_f = K[H^+]^n$ ou $\log K_f = \log K - n$ pH.

Le tableau 2 donne les variations de K_f avec le pH, à 298 K.

La figure 2 représente le graphe $\log K_f = f(\text{pH})$. Au-dessus de pH 5, c'est une droite de pente -2. La pente diminue (en valeur absolue) en milieu plus acide, ce qui s'explique par l'intervention de l'équilibre:

$$B^{2-} + H^+ \rightleftharpoons HB^- \quad (pK_2 = 2,70)$$

La réaction de complexation s'écrit donc:

$$MoO_4^{2-} + B^{2-} + 2H^+ \rightleftharpoons X'$$

L'extrapolation à l'origine du segment de droite de pente -2 donne $\log K = 13,60$ d'où: $K = 4.10^{13}$.

Equilibre entre X et X'. Cet équilibre s'observe entre pH 1 et pH 4, zone dans laquelle Mo(VI) forme des polyanions et n'intervient donc pas dans l'équation de formation de façon simple. Aussi avons-nous complexé l'ion bromanilate par un excès de molybdate (de façon à obtenir 100% de complexation à tout pH) et fait varier le pH.

La présence de deux points isosbestiques.

$$\lambda = 356\text{ nm},\quad \epsilon = 1,38.10^4\ \text{l.mole}^{-1}.\text{cm}^{-1}$$

$$\lambda = 321\text{ nm},\quad \epsilon = 1,34.10^4\ \text{l.mole}^{-1}.\text{cm}^{-1}$$

prouve l'absence d'une troisième espèce, l'absorbance de Mo(VI) étant négligeable.

Tableau 2. Variation de la constante conditionnelle de complexation avec le pH (I = 0,20M; T = 298 K)

pH	4,40	4,60	4,80	5,00	5,25	5,40	5,60
K_f	$3,58.10^4$	$1,84.10^4$	$8,00.10^3$	$4,00.10^3$	$1,08.10^3$	535	250

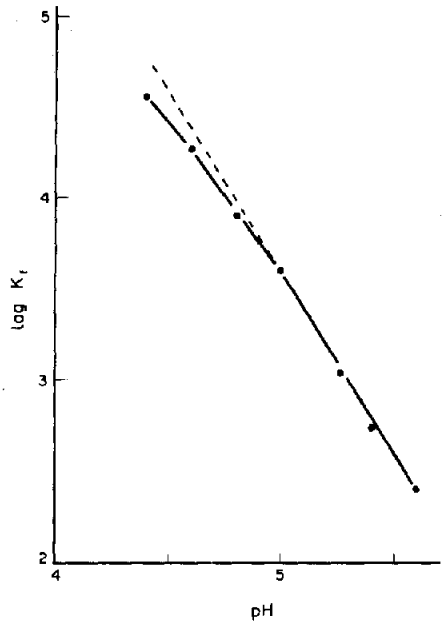


Fig. 2. Variation de la constante conditionnelle avec le pH. $[B^{2-}]_T = [MoO_4^{2-}]_T = 5.10^{-4}M$; $T = 298$ K; tampon acétique 0,20M.

La figure 3 montre les spectres des deux complexes comparés à celui de l'ion B^{2-}. Nous avons calculé par spectrophotométrie les proportions des deux complexes en fonction du pH. Le pK a été déterminé par la relation:

$$pK = pH + \log \frac{[X]}{[X']}.$$

Les résultats sont donnés dans le tableau 3.

La valeur constante trouvée ($pK = 2{,}30 \pm 0{,}05$) confirme l'intervention d'un seul proton dans l'équilibre.

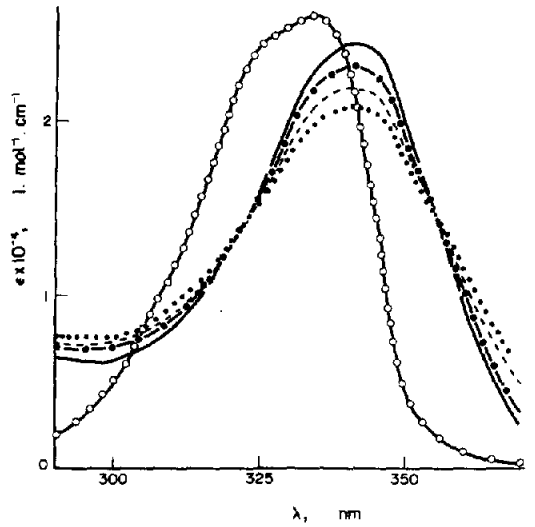


Fig. 3. Spectres dans l'ultraviolet de B^{2-} et des deux complexes molybdiques. $[B^{2-}]_I = 5.10^{-4}M$; $[Mo(VI)]_T = 2.10^{-3}M$. O—O—O: pH ≥ 9: B^{2-}; ——: pH = 4,05: $(1,1,2)^{2-}$; — · — · —: pH = 2,58; -----: pH = 2,00; · · · · ·: pH = 0,85: $(1,1,3)^{-}$.

Tableau 3. Détermination du pK du complexe

pH	ε, $l.mole^{-1}.cm^{-1}$	[X], %	[X'], %	log [X]/[X']	pK
0,85	$2,06.10^4$	100	0		
1,50	$2,11.10^4$	87	13	+0,82	2,32
1,75	$2,15.10^4$	76	24	+0,50	2,25
2,00	$2,18.10^4$	68	32	+0,33	2,33
2,25	$2,23.10^4$	55	45	+0,09	2,34
2,50	$2,29.10^4$	39,5	60,5	−0,19	2,31
2,75	$2,34.10^4$	26	74	−0,45	2,30
3,00	$2,38.10^4$	16	84	−0,72	2,28
>4	$2,44.10^4$	0	100		

Conditions: $[H_2B]_T = 5.10^{-4}M$, $[Mo(VI)]_T = 2.10^{-3}M$; ε mesuré à 340 nm; $I = 0{,}20M$; $T = 298$ K.

Par la suite, le complexe X', qui est formé à partir d'un ion molybdate MoO_4^{2-}, d'un ion bromanilate B^{2-} et de deux protons, sera désigné par $(1,1,2)^{2-}$. Le complexe X, qui en dérive par fixation d'un proton, s'écrira $(1,1,3)^{-}$. Cette écriture ne tient pas compte des molécules d'eau éventuellement présentes dans ces complexes pour compléter à six la coordinence du molybdène.

Spectres électroniques des complexes. Le tableau 4 résume les bandes d'absorption des espèces H_2B, HB^-, B^{2-}, $(1,1,3)^-$ et $(1,1,2)^{2-}$.

Comme le montre la figure 3, les spectres dans l'ultraviolet des complexes $(1,1,3)^-$ et $(1,1,2)^{2-}$ sont voisins de celui de l'ion B^{2-}. La forte intensité des bandes dans l'ultraviolet est caractéristique de la délocalisation de l'ion B^{2-}. Nous en concluons que le ligand conserve une structure délocalisée dans le complexe. La diminution d'intensité des bandes dans l'ultraviolet des complexes montre que la résonance est moins importante que dans l'ion B^{2-} libre. Par contre, on note que l'intensité de la bande des complexes (dans le visible) est proche de celle de l'ion HB^-. L'absorbance dans le visible semble liée à la présence de doublets localisés sur certains atomes d'oxygène.

Le spectre du complexe $(1,1,3)^-$ est très voisin de celui des complexes bromaniliques de Zr(IV) et Hf(IV) formés en milieu $HClO_4$ 2,8M.[6] La modification du spectre dans l'ultraviolet de l'ion B^{2-} n'est donc pas spécifique de la nature du cation complexé, mais correspond à un changement de la structure électronique du ligand.

D'autre part, il est remarquable que les intensités des bandes dans le visible et l'ultraviolet varient en

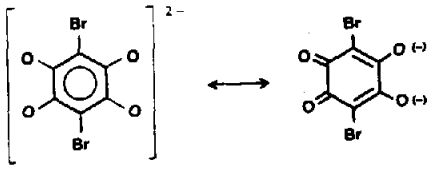
Tableau 4. Spectres électroniques des espèces bromaniliques libres et complexées

	λ, nm	ε, $l.mole^{-1}.cm^{-1}$	λ, nm	ε, $l.mole^{-1}.cm^{-1}$
H_2B	311,5	$1,80.10^4$	455	230
HB^-	315	$1,60.10^4$	522,5	870
B^{2-}	334	$2,65.10^4$	520	190
$(1,1,2)^{2-}$	340	$2,44.10^4$	550	680
$(1,1,3)^-$	340	$2,06.10^4$	550	915

sens inverse dans l'ordre:

$$B^{2-},\ (1,1,2)^{2-},\ (1,1,3)^{-},\ HB^{-}$$

Il semble que la protonation de $(1,1,2)^{2-}$ se traduise par une perte d'aromaticité du ligand, le proton fixé venant accroître la charge positive du groupement molybdique et donc la polarisation du ligand. Comme pour les complexes chloraniliques de Mo(VI),[5] nos résultats s'interprètent par une augmentation du poids de la forme limite **III** dans la structure mésomère **II** du ligand B^{2-}.



II **III**

Conclusion. Comme le système C^{2-}–H^{+}–Mo(VI),[5] le système B^{2-}–H^{+}–Mo(VI) forme deux complexes 1:1

$$HMoO_3^{+} + H_2B + H_2O \rightleftharpoons (1,1,3)^{-} + 2H^{+} \qquad (H^{+}) > 0{,}5M$$

$$(1,1,3)^{-} \rightleftharpoons (1,1,2)^{2-} + H^{+} \qquad pK = 2{,}30$$

$$(1,1,2)^{2-} \rightleftharpoons MoO_4^{2-} + B^{2-} + 2H^{+} \qquad pH > 4$$

Les valeurs de pK des complexes de B^{2-} et C^{2-} sont identiques aux erreurs expérimentales près, bien que les valeurs de pK de H_2B et H_2C diffèrent de 0,2 unité de pH.

Les constantes apparentes de formation des complexes $(1,1,2)^{2-}$ sont voisines:

$$K = 8.10^{13} \text{ pour } H_2C^{5} \text{ et } 4.10^{13} \text{ pour } H_2B$$

La différence n'est pas suffisamment significative pour comparer l'affinité des deux oxocarbones pour Mo(VI) en fonction de leur basicité. Les résultats de l'étude en solution, confirmés par l'étude (par spectroscopie dans l'infra-rouge) du complexe molybdique de l'ion bromanilate.[12] permettent d'attribuer aux complexes bromanilique et chloranilique de Mo(VI) des structures analogues.

Dosage de Mo(VI) par l'acide bromanilique en milieu perchlorique très acide

Principe du dosage. Mo(VI) peut être dosé par spectrophotométrie,[8] sans réduction préalable, en formant le complexe chloranilique $(1,1,3)^{-}$ en milieu $HClO_4$ 1,4M. Bien que la stabilité du complexe soit faible à une telle acidité, il est avantageux d'utiliser ce milieu, dans lequel les interférences dues aux cations métalliques non hydrolysés sont minimisées. L'acidité retenue est un compromis entre la sélectivité et la sensibilité de la méthode.

Nous avons trouvé que le complexe $(1,1,3)^{-}$ bromanilique était plus stable en milieu très acide que son homologue chloranilique. Etant donné que les deux complexes ont pratiquement la même absorbance à 340 nm (λ max), il semblait possible d'accroître la précision du dosage de Mo(VI) en substituant H_2B à H_2C. En effet, la plus grande proportion de complexe formée devait permettre d'augmenter l'acidité (d'où un gain de sélectivité) sans perdre en sensibilité.

Afin de chiffrer quantitativement le gain de précision possible, nous avons réalisé dans les mêmes conditions le dosage spectrophotométrique de Mo(VI) par H_2B et H_2C. Le degré de complexation est alors important et permet de calculer avec une bonne précision les constantes conditionnelles de formation des deux complexes.

A deux acidités fixées ($HClO_4$ 3M et 1,4M), nous avons ajouté des quantités connues de Mo(VI) à un excès d'acide bromanilique. Puis nous avons tracé les droites $A = f([Mo(VI)]_T)$ en nous limitant aux conditions telles que la loi de Beer-Lambert soit suivie. Chaque droite correspond à un excès connu d'acide bromanilique et la valeur de leurs pentes permet de calculer la constante conditionnelle de formation du complexe, qui a été comparée à celle obtenue avec H_2C dans les mêmes conditions.

La méthode utilisée pour le calcul des K_f est dérivée de la méthode du rapport des pentes (slope ratio method)[13] dans le cas particulier où la formation du complexe n'est pas quantitative. Un exemple de calcul est détaillé ci-dessous.

Réactif H_2B dans $HClO_4$ 3M. A $\lambda = 340$ nm ($l = 1{,}00$ cm), les variations de l'absorbance en fonction de la concentration analytique de Mo(VI) suivent la loi de Beer-Lambert jusqu'à $[Mo(VI)]_T = 10^{-4}M$ quand $[H_2B]_T$ varie de 5.10^{-4} à $2.10^{-3}M$.

Les droites expérimentales ont pour équations:

$$[H_2B]_T = 5.10^{-4}M \qquad A = 0{,}200 + 4{,}18.10^{3}[Mo(VI)]_T$$

$$[H_2B]_T = 10^{-3}M \qquad A = 0{,}400 + 6{,}65.10^{3}[Mo(VI)]_T$$

$$[H_2B]_T = 2.10^{-3}M \qquad A = 0{,}790 + 9{,}75.10^{3}[Mo(VI)]_T$$

On en tire les valeurs de α [proportion de Mo(VI) complexé] de la manière suivante. L'acidité étant constante, la réaction de complexation apparente peut s'écrire:

$$Mo(VI) + H_2B \rightleftharpoons X$$

A l'équilibre, les concentrations sont:

$$[X] = \alpha[Mo(VI)]_t$$

et

$$[Mo(VI)] = (1 - \alpha)\,[Mo(VI)]_T$$

et puisque H_2B est en excès:

$$[H_2B] = [H_2B]_T$$

Tableau 5. Calcul de K_f pour le complexe H_2B–Mo(VI) en milieu $HClO_4$ 3*M*

$[H_2B]_T$, *M*	*p. l/mole*	α	K_f
2.10^{-3}	$9{,}75.10^3$	0,47	443
10^{-3}	$6{,}65.10^3$	0,32	470
$0{,}5.10^{-3}$	$4{,}18.10^3$	0,20	500

λ = 340 nm; l = 1,00 cm; $\epsilon_X = 2{,}06.10^4$ l.mole^{-1}.cm^{-1}; T = 298 K.

Seules les espèces H_2B et X absorbent. L'absorbance A des solutions est donnée par:

$$A = \epsilon_{H_2B}\, l[H_2B]_T + \epsilon_X\, l\,\alpha[Mo(VI)]_T$$

ϵ_{H_2B} = absorbance molaire de H_2B

ϵ_X = absorbance molaire du complexe $(1,1,3)^-$

On vérifie bien que le premier terme est proportionnel à $[H_2B]_T$ avec $\epsilon_{H_2B} = 400$ l.mole^{-1}.cm^{-1}.

La pente des droites vaut donc $p = \epsilon_X l\alpha$.

L'absorbance ϵ_X a été déterminée dans la première partie de ce travail: $\epsilon_X = 2{,}06.10^4$ l.mole^{-1}.cm^{-1}.

On peut ainsi calculer α qui est relié à K_f:

$$K_f = \frac{[X]}{[Mo(VI)][H_2B]} = \frac{\alpha}{1-\alpha}\cdot\frac{1}{[H_2B]_T}.$$

Les résultats sont résumés dans le Tableau 5.

Réactif H_2C dans $HClO_4$ 3M. Les droites expérimentales (λ = 340 nm, l = 1,00 cm) ont pour équations:

$[H_2C]_T = 5.10^{-4}M$

$A = 0{,}100 + 2{,}68.10^3[Mo(VI)]_T$

$[H_2C]_T = 10^{-3}M$

$A = 0{,}200 + 4{,}60.10^3[Mo(VI)]_T$

Les calculs de α et K_f sont donnés dans le Tableau 6.

Discussion. La précision des résultats est suffisante pour mettre en évidence la plus grande stabilité du complexe bromanilique: $K_f = 470 \pm 30$ (H_2B) contre $K_f = 286 \pm 10$ (H_2C).

L'augmentation de sensibilitié due au changement de réactif peut être mesurée par la valeur de la pente p:

$[H_2C]_T = 10^{-3}M$; p = 4600 l.mole^{-1}

$[H_2B]_T = 10^{-3}M$; p = 6650 l.mole^{-1}

La concentration de Mo(VI) qui provoque un accroissement d'absorbance de 0,1 (quand l = 1 cm) est de:

$1{,}50.10^{-5}M$ (ou 1,44 mg/l.) pour H_2B $10^{-3}M$

$2{,}17.10^{-5}M$ (ou 2,08 mg/l.) pour H_2C $10^{-3}M$

Le maximum de sensibilité est obtenu pour $[H_2B]_T = 2.10^{-3}M$. Mais à cette concentration, l'absorbance propre du réactif est élevée à 340 nm et il est avantageux de se placer à λ = 350 nm, où la précision est encore bonne. L'équation de la droite est alors:

$$A = 0{,}360 + 7{,}40.10^3[Mo(VI)]_T$$

Nous avons ensuite cherché si un gain de sensibilité équivalent était obtenu en milieu $HClO_4$ 1,4*M*, ce qui était le milieu optimal de dosage en utilisant H_2C.[8] En effet, une diminution de l'acidité doit se traduire par l'augmentation des valeurs de K_f des deux complexes.

Résultats dans $HClO_4$ 1,4M. Nous avons tracé comme ci-dessus les droites $A = f[Mo(VI)]_T$ pour H_2C et H_2B à la concentration $10^{-3}M$. Elles ont pour équations:

H_2C $A = 0{,}305 + 1{,}35.10^4[Mo(VI)]_T$

H_2B $A = 0{,}530 + 1{,}54.10^4[Mo(VI)]_T$

Les résultats et le calcul des constantes conditionnelles sont regroupés dans le tableau 7.

On constante immédiatement que les pentes des droites sont plus fortes qu'en milieu $HClO_4$ 3*M*, ce qui indique une meilleure sensibilité (due à la croissance de α). Mais la différence de sensibilité (mesurée par le rapport des pentes Δp) a diminué. Par contre, le rapport des constantes conditionnelles ΔK_f reste constant.

—dans $HClO_4$ 1,4*M* Δp = 1,145; ΔK_f = 1,60
—dans $HClO_4$ 3*M* Δp = 1,446; ΔK_f = 1,64

La concentration de Mo(VI) qui provoque un accroissement d'absorbance de 0,1 (quand l = 1 cm) est de:

$7{,}43.10^{-6}M$ (ou 0,71 mg/l.) pour H_2C $10^{-3}M$
$6{,}49.10^{-6}M$ (ou 0,63 mg/l.) pour H_2B $10^{-3}M$

Dosage d'échantillons contenant du molybdène: interférences. Etant donné la similitude des propriétés chimiques de H_2C et H_2B, il est possible de reprendre sans modifications le mode opératoire de Waterbury et Bricker[8] qui effectuent l'extraction du molybdène(VI) par la 4-méthyl-2-pentanone (MIBK; hexone), puis une contre-extraction par l'eau. Un traitement par une solution d'hydroxyde de sodium élimine alors la

Tableau 6. Calcul de K_f pour le complexe H_2C–Mo(VI) en milieu $HClO_4$ 3*M*

$[H_2C]_T$, *M*	*p. l/mole*	α	K_f
10^{-3}	$4{,}60.10^3$	0,219	281
$0{,}5.10^{-3}$	$2{,}68.10^3$	0,127	291

λ = 340 nm; l = 1,00 cm; $\epsilon_X = 2{,}10.10^4$ l.mole^{-1}.cm^{-1}; T = 298 K.

Tableau 7. Calcul de K_f pour les complexes de Mo(VI) avec H_2B et H_2C dans $HClO_4$ 1,4*M*

réactif, $10^{-3}M$	*p. l/mole*	α	K_f
H_2C	$1{,}35.10^4$	0,64	$1{,}78.10^3$
H_2B	$1{,}54.10^4$	0,74	$2{,}85.10^3$

λ = 340 nm; l = 1,00 cm; T = 298 K.

plupart des cations métalliques bivalents [et le fer (III) si l'échantillon était un acier].

Les éléments gênants sont ceux qui donnent des oxo-ions solubles à la fois en milieu alcalin et acide. Nous avons observé que les ions suivants interféraient: Zr(IV), Hf(IV), U(VI), Cr(VI), V(V) et W(VI). D'après la référence 8, l'étain et le bismuth gênent aussi.

Conclusion. Nous avons trouvé que le gain de sensibilité dû au remplacement de H_2C par H_2B augmente avec la molarité de l'acide perchlorique, tandis que la sensibilité des deux réactifs diminue par suite de leur masquage par les protons. Cette observation explique les résultats apparemment contradictoires des travaux antérieurs sur l'utilité analytique de l'acide bromanilique. En milieu où la molarité des protons est inférieure à 2*M*, il ne permet pas de dosages plus précis que l'acide chloranilique.[7] Au contraire, il se révèle un meilleur réactif en milieu plus acide, par exemple dans le dosage du zirconium-(IV) en milieu $HClO_4$ 2.8*M*.[6]

On peut relier la meilleure sensibilité de H_2B dans les milieux très acides à son pK_1 inférieur à celui de H_2C. En effet, la formation des complexes dépend de la facilité avec laquelle les acides (de pouvoir complexant nul) s'ionisent en hydrogénoions HB^- ou HC^-, les ions B^{2-} et C^{2-} n'existant pas en milieu $HClO_4 > 1M$. Pour cela, on met l'équation de formation des complexes $(1,1,3)^-$ sous la forme suivante, qui fait apparaître les hydrogénoions:

$$HMoO_3^+ + HB^- \text{ (ou } HC^-) \rightleftharpoons (1,1,3)^- + H^+$$

Dans le cas de HB^-, la constante apparente de cet équilibre est:

$$K' = \frac{[(1,1,3)^-][H^+]}{[HMoO_3^+][HB^-]}$$

En milieu très acide, $[HB^-] \ll [H_2B]$ et $[HB] = K_1[H_2B]_T/[H^+]$, K_1 étant la première constante d'ionisation de H_2B.

$$K_f = \frac{[(1,1,3)^-]}{[HMoO_3^+][H_2B]} = K'K_1/[H^+]^2$$

On fait un calcul identique dans le cas de HC^-. Le rapport des constantes conditionnelles de complexation des deux réactifs est alors indépendant de l'acidité:

$$\frac{K_f(H_2B)}{K_f(H_2C)} = \frac{K'(H_2B)}{K'(H_2C)} \cdot \frac{K_1(H_2B)}{K_1(H_2C)}$$

D'après nos résultats antérieurs[5] et ceux de ce travail, le rapport des K_1 est:

$$\frac{K_1(H_2B)}{K_1(H_2C)} = \frac{0{,}600}{0{,}355} = 1{,}69 \pm 0{,}10$$

et le rapport

$$\frac{K_f(H_2B)}{K_f(H_2C)} = 1{,}62 \pm 0{,}04.$$

On en déduit que les deux constantes K' [constantes de complexation de Mo(VI) par HC^- et HB^-] sont égales aux incertitudes près. D'autre part, entre pH 4 et 6, nous n'avons pas trouvé de différences significatives entre les constantes de formation des complexes $(1,1,2)^{2-}$ à partir des ions C^{2-} et B^{2-}.

Ces résultats viennent confirmer la relation[14] établie par Beauchamp et Benoit entre les constantes de stabilité des complexes formés par cinq hydroxyquinones substituées (dont H_2C) avec le germanium (IV) et la somme des pK de ces complexants.

A partir de nos mesures, on calcule:

pour H_2C[5] $pK_1 + pK_2 = 0{,}45 + 2{,}50 = 2{,}95$

pour H_2B $pK_1 + pK_2 = 0{,}22 + 2{,}70 = 2{,}92$

La basicité totale des deux ions B^{2-} et C^{2-} est la même et justifie donc l'égalité de leurs pouvoirs complexants.

En conclusion, la différence de comportement entre H_2B et H_2C en milieu très acide provient uniquement de la différence de leur valeurs de pK_1. L'ion C^{2-} est masqué par les protons avant l'ion B^{2-}. En conséquence, il n'est avantageux de remplacer H_2C par H_2B qu'en milieu acide de normalité supérieure à 2*N*. Aux acidités inférieures, les deux réactifs ont la même basicité et sont des agents complexants de force identique.

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Summary—The bromanilate ion B^{2-} is a cyclic aromatic anion related to oxocarbons. We have shown by ultraviolet–visible spectrophotometry that it forms two 1:1 complexes with molybdenum(VI) in aqueous solution at pH ≤ 6. The variation of the conditional stability constants with acidity allows

the calculation of the number of protons involved in each equilibrium. The formulae of the two complexes differ by a proton. The pK is 2.30. Molybdenum(VI) can be determined with bromanilic acid, H_2B, at 340 nm in 3 or 1.4M perchloric acid. The accuracy is better than with chloranilic acid, H_2C, when the concentration is about 1 mg/l. The better results obtained with H_2B at high acidities are accounted for by the difference between the pK_1 values of the two acids (0.22 for H_2B and 0.45 for H_2C).

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APPLICATIONS ANALYTIQUES DES OXOCARBONES—II

COMPOSITION DES COMPLEXES TUNGSTIQUES DES IONS BROMANILATE ET CHLORANILATE: DOSAGE SPECTROPHOTOMETRIQUE DU TUNGSTENE(VI)

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Résumé—Les complexes formés entre le tungstène(VI) et les ions chloranilate C^{2-} et bromanilate B^{2-} ont été étudiés en solution aqueuse et à l'état solide, par spectroscopie (ultra-violet, visible et infra-rouge). A pH 3–4, les complexes ont une stoechiométrie ligand:tungstène = 2. A pH < 2 il n'apparaît que des complexes 1:1. Les deux réactifs permettent le dosage spectrophotométrique de W(VI) (λ = 335 nm pour H_2C et 340 nm pour H_2B) en milieu $HClO_4$ 1,4*M* à des concentrations voisines de 1 mg/l. Les constantes conditionnelles de formation des deux complexes 1:1 dans ce milieu ont été calculées. Les complexes tungstiques sont plus stables que les complexes molybdiques correspondants, et les complexes de B^{2-} sont plus stables que les complexes de C^{2-} [avec W(VI) comme avec Mo(VI)]. On montre que l'écart provient de la différence des valeurs de pK_1 des acides H_2B et H_2C. Les spectres (dans l'infra-rouge) des complexes de B^{2-} et C^{2-} avec Mo(VI) et W(VI) sont discutés en vue de préciser l'interaction entre les ions métalliques et les ligands aromatiques.

Les acides chloranilique (dichloro-2,5-dihydroxy-3,6-benzoquinone-1,4: H_2C) et bromanilique (dibromo-2,5-dihydroxy-3,6-benzoquinone-1,4: H_2B) s'ionisent en ions C^{2-} et B^{2-} dans lesquels les deux charges négatives sont délocalisées sur les quatre atomes d'oxygène:

X = Cl H_2C
X = Br H_2B
C^{2-} ion chloranilate
B^{2-} ion bromanilate.

Les deux ions aromatiques sont apparentés aux oxocarbones[1] et constituent des agents complexants remarquables en milieu fortement acide. Ils permettent le dosage spectrophotométrique sélectif des ions métalliques de haut degré d'oxydation. Par contre, la plupart des cations métalliques non hydrolysés sont précipités sous forme de chélates insolubles dans tous les solvants usuels.

Nous avons récemment étudié[2,3] les complexes formés entre les ions B^{2-} et C^{2-} et les ions de Mo(VI) en solution acide. Les constantes conditionnelles[4] de formation des complexes 1:1 varient comme la première constante d'ionisation des deux acides. L'acide bromanilique, étant le plus fort,[3] est le réactif le plus sensible pour le dosage du molybdène(VI).

Le présent travail a pour but d'examiner les possibilités de dosage spectrophotométrique du tungstène(VI) par les deux oxocarbones B^{2-} et C^{2-}. Malgré l'analogie apparente des propriétés des ions Mo(VI) et W(VI), la méthode utilisée précédemment pour l'étude des complexes molybdiques[2,3] s'est avérée inapplicable. En effet, on ne peut pas exploiter les variations des constantes conditionnelles de formation des complexes tungstiques avec le pH, car le tungstène(VI) libre se condense[5] lentement et de manière irréversible en-dessous de pH 7.

Nous nous sommes donc limités à déterminer la composition des complexes tungstiques de B^{2-} et C^{2-} en solution à différents pH par spectrophotométrie dans l'ultra-violet–visible. Nous avons ensuite cherché les conditions convenables pour le dosage spectrophotométrique du tungstène(VI) en milieu acide perchlorique, en utilisant les deux réactifs H_2B et H_2C. Enfin, nous discutons la nature des complexes formés, à partir de leurs spectres électroniques, et du spectre infra-rouge de composés solides que nous avons préparés par réaction de H_2B et H_2C avec les ions tungstate. Nous montrons que les complexes bromaniliques et chloraniliques de W(VI) et de Mo(VI) constituent une famille distincte des polymères de coordination formés par ces oxocarbones avec la plupart des cations métalliques.[6,7]

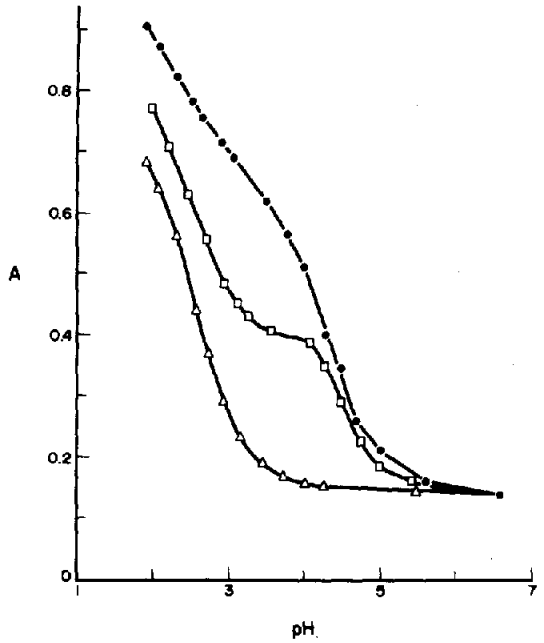


Fig. 1a. Système H^+–B^{2-}–W(VI). Variation de l'absorbance en fonction du pH. $[H_2B]_T = 10^{-3}M$; tampon formique $1M$; $l = 1{,}00$ cm; $\lambda = 560$ nm; $q = [W(VI)]_T/[B^{2-}]_T$. ●●●● $q = 2{,}0$; □□□ $q = 0{,}5$; △△△ $q = 0{,}0$.

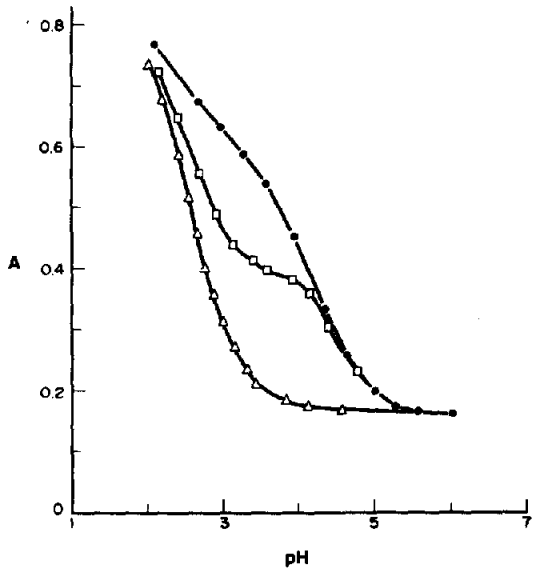


Fig. 1b. Système H^+–C^{2-}–W(VI). Variation de l'absorbance en fonction du pH. $[H_2C]_T = 10^{-3}M$; tampon formique $1M$; $l = 1{,}00$ cm; $\lambda = 560$ nm; $q = [W(VI)]_T/[C^{2-}]_T$. ●●●● $q = 2{,}0$; □□□ $q = 0{,}5$; △△△ $q = 0{,}0$.

PARTIE EXPERIMENTALE

Appareils, produits et notations

Ce sont ceux utilisés dans l'article précédent.[3] Les spectres infra-rouge ont été enregistrés sur un Beckman IR-12, les produits solides étant dilués dans des pastilles de KBr.

Solution de W(VI). Le tungstate de sodium était un produit Prolabo R.P. On a préparé par pesée une solution-mère 0,100M en WO_4^{2-}, dans la soude 0,01N. On a vérifié que les ions WO_4^{2-} ne se condensaient pas dans ce milieu, en dosant périodiquement la solution-mère par spectrophotométrie, après formation du complexe W(VI): dihydroxy-1,2-benzène, en tampon acétique de pH 5. L'étalonnage a été réalisé avec des masses pesées de $Na_2WO_4.2H_2O$. Ce dosage donne la concentration des seules espèces tungstiques labiles, les formes polymérisées réagissant trop lentement pour interférer.[8]

Précautions opératoires. L'obtention de résultats reproductibles exige le respect du mode opératoire suivant: on introduit successivement dans une fiole le tampon, puis le ligand et enfin le tungstate. La complexation est alors rapide et le complexe reste stable plusieurs jours. Au contraire, quand le tungstate est introduit dans le tampon en l'absence de ligand, il se condense partiellement et la réaction de complexation devient lente et incomplète.

Préparation des complexes solides

La méthode générale de préparation est dérivée de celle décrite antérieurement[2] pour le complexe H_2C–Mo(VI). On mélange 1 mmole du réactif organique dissoute dans 50 ml de méthanol et 1 mmole de tungstate (ou de molybdate) de sodium dissoute dans 10 ml d'eau distillée. On évapore totalement le solvant sous pression réduite (20 mmHg) à 313 K. Le solide est ensuite mis en suspension dans l'acétone qui dissout l'excès éventuel de dihydroxyquinone.

On filtre le solide sur verre fritté de porosité n° 4, et on le lave à l'acétone jusqu'à ce que le filtrat soit incolore. On le sèche enfin à l'étuve à 333 K pour chasser l'acétone adsorbée. Le rendement est supérieur à 80%.

(*a*) Complexe chloranilique de W(VI).
Poudre mauve hygroscopique analyse WO_3, $C_6O_4Cl_2$, 2Na, $3H_2O$ $M = 538{,}85$

	C, %	H, %	Cl, %
trouvé	13,6	1,6	13,6
calculé	13,40	1,11	13,20

Masse molaire mesurée: $M = 538 \pm 5$

(*b*) Complexe bromanilique de W(VI)
Poudre mauve hygroscopique analyse WO_3, $C_6O_4Br_2$, 2Na, $4H_2O$ $M = 645{,}79$

	C, %	H, %	Br, %
trouvé	10,9	1,5	25,8
calculé	11,16	1,25	24,74

Masse molaire mesurée: $M = 635 \pm 10$
La valeur 645 correspond à 4 H_2O
La valeur 627 correspond à 3 H_2O

(*c*) Complexe bromanilique de Mo(VI)
Poudre bleu foncé, hygroscopique analyse MoO_3, $C_6O_4Br_2$, 2Na, $3H_2O$ $M = 539{,}86$

	C, %	H, %	Br, %
trouvé	13,5	2,2	30,2
calculé	13,35	1,12	29,60

Masse molaire mesurée: $M = 519 \pm 5$
(correspond au dihydrate, théorique 521,84)

Les microanalyses ont été réalisées au Laboratoire de Microanalyse, Université de Paris VI, par M. Dorme que nous remercions.

La masse molaire des produits a été déterminée en dissolvant une masse connue (environ 20 mg) dans 100 ml de tampon hydrogénocarbonate à pH 7,50 et en dosant par spectrophotométrie (ultra-violet) l'ion B^{2-} ou C^{2-} libéré. La masse molaire a été rapportée à un ion bromanilate ou chloranilate.

RESULTATS ET DISCUSSION

Composition des complexes tungstiques de B^{2-} et C^{2-} en solution acide

Dans tout milieu compris entre $HClO_4$ 1,4M et pH 6, l'introduction d'ions de W(VI) dans une solu-

tion de H_2B ou de H_2C fait virer la couleur vers le violet. La modification correspondante du spectre dans l'ultra-violet des réactifs est peu importante. Aussi avons-nous travaillé surtout sur les bandes visibles où les différences dues à la complexation sont plus marquées.

Zone d'existence des complexes. Les figures 1a et 1b représentent les variations de l'absorbance à $\lambda = 560$ nm en fonction du pH pour des solutions de rapport fixé $q = [W(VI)]_T/[\text{réactif}]_T$, le réactif étant respectivement H_2B et H_2C.

Les courbes correspondant à $q = 0{,}5$ montrent l'existence d'un premier complexe vers pH 2, et d'un second dans la zone de pH 3–4. Ce dernier se dissocie aux pH supérieurs en redonnant l'anion B^{2-} ou C^{2-}.

Les courbes tracées pour $q = 2{,}0$ ne comportent plus de palier entre pH 3 et 4. Un excès de tungstate favorise donc la formation d'un complexe de rapport stoechiométrique supérieur à 0,5.

Complexes formés entre pH 3 et 4. A pH 4, les variations de l'absorbance de solutions d'ions B^{2-} et C^{2-} en fonction de l'addition de W(VI) indiquent la formation exclusive d'un complexe de rapport $q = 0{,}5$. Les courbes des figures 2a et 2b ont été tracées à $\lambda = 560$ nm.

Une étude similaire effectuée sur la bande ultra-violette ($\lambda = 330$–335 nm) des ions B^{2-} et C^{2-} montre que les complexes 1:2 ont des absorbances proches de celles des ligands libres. Tous les spectres sont rassemblés dans les tableaux 2 et 3.

Complexes formés aux pH inférieurs à 3. Entre pH 2,0 et 2,5 les différences spectrales sont plus nettes dans l'ultra-violet que dans le visible. Nous avons tracé les courbes $A = f[W(VI)]_T$ qui présentent une cassure arrondie pour $q = 1$, dans le cas des deux réactifs. Cependant, la partie initiale de ces courbes est déformée, ce qui laisse soupçonner la formation préliminaire du complexe 1:2 détecté en milieu moins acide.

Les spectres des complexes 1:1 [formés quantitativement en présence d'un excès de W(VI)] sont différents des spectres des complexes 1:2 (Tableaux 2 et 3).

Nous avons remarqué qu'un accroissement de la force ionique favorise la formation initiale du complexe 1:2. Nous avons pu ainsi la mettre en évidence dans un tampon formique 3*M* de pH 2,50. Le tableau 1 montre que la concentration d'acide chloranilique complexé est constamment supérieure à la concentration analytique du tungstène(VI), tant que le rapport q est inférieur à 1.

On constate donc que les deux complexes 1:1 et 1:2 coexistent dans cette zone de pH. Puisqu'une augmentation de l'acidité favorise le complexe 1:1 aux

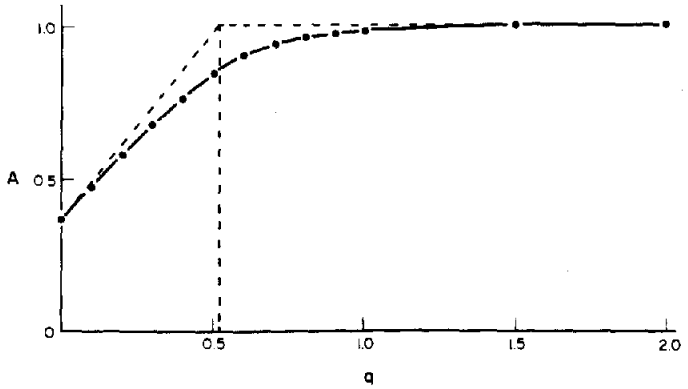


Fig. 2a. Composition du complexe bromanilique de W(VI) à pH = 3,99. $[H_2B]_T = 2.10^{-3}M$; $q = [W(VI)]_T/[B^{2-}]_T$; $l = 1{,}00$ cm; $\lambda = 560$ nm; tampon acétique 1*M*.

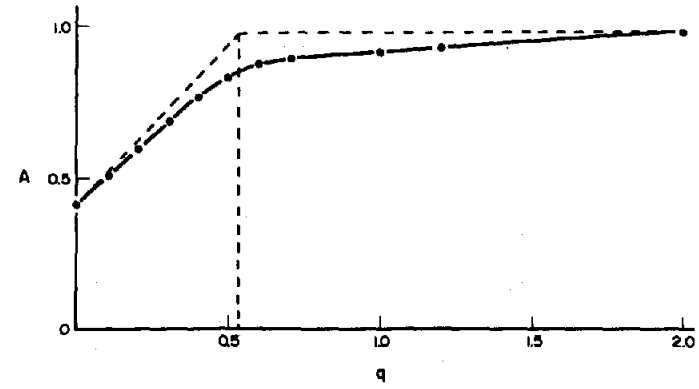


Fig. 2b. Composition du complexe chloranilique de W(VI) à pH = 4,03 $[H_2C]_T = 2.10^{-3}M$; $q = [W(VI)]_T/[C^{2-}]_T$; $l = 1{,}00$ cm; $\lambda = 560$ nm; tampon acétique 1*M*.

Tableau 1. Proportion de H_2C complexé à pH 2,50

$[W(VI)]_T$, $10^{-4}M$	1,00	2,00	3,00	4,00	5,00	6,00	8,00	10,00
$[H_2C]$ complexé, $10^{-4}M$	1,33	2,53	3,74	4,80	5,73	6,53	8,26	9,46

$[H_2C]_T = 10^{-3}M$; $T = 298$ K; tampon formique $3M$.

dépens du 1:2, l'étude du complexe 1:1 a été poursuivie en milieu acide $1N$.

En milieu $HClO_4$ $1M$, le complexe 1:2 n'est plus décelable et on ne détecte qu'un complexe 1:1, dont le pourcentage de formation est moins élevé qu'à pH 2.

Il n'est plus possible de déterminer directement le spectre de ce complexe en présence d'un excès de W(VI) car le tungstate libre précipite sous forme d'acide H_2WO_4 (ou $WO_3.nH_2O$). Nous l'avons donc estimé en multipliant par 10 la variation d'absorbance trouvée quand $q = 0{,}1$. L'absorbance calculée ainsi à plusieurs longueurs d'onde est inférieure à celle du complexe 1:1 formé à pH 2, mais lui est exactement proportionnelle. On en conclut qu'il s'agit du même complexe.

Discussion. Le tungstène(VI) forme deux types de complexes avec les deux dihydroxyquinones étudiées:

—à pH < 3 des composés 1:1,

—à pH > 3 des composés 1:2.

Ce comportement est analogue à celui décrit[9] dans la réaction de l'uranium(VI) (qui existe sous forme d'ions uranyle UO_2^{2+}) avec l'acide chloranilique. Par contre, le molybdène(VI) se distingue des autres ions de la colonne VIB de la classification périodique en ne formant que des complexes 1:1 avec H_2C^2 et H_2B.[3]

Spectres électroniques des complexes

Les spectres des acides, de leurs ions et des complexes tungstiques sont décrits dans le tableau 2 pour H_2B et dans le tableau 3 pour H_2C.

On constate que les bandes dans l'ultra-violet des ions B^{2-} et C^{2-} et de leurs complexes tungstiques se situent à des longueurs d'onde identiques, ce qui montre que les ligands conservent un important caractère aromatique dans les complexes. L'intensité de la bande diminue dans l'ordre B^{2-} ou C^{2-} > complexe 1:2 > complexe 1:1. Les complexes de W(VI) absorbent dans l'ultra-violet à des longueurs d'onde inférieures à celles des complexes de Mo(VI): respectivement 337 nm avec C^{2-} et 340 nm avec B^{2-}. Comme les complexes molybdiques, les complexes de W(VI) absorbent dans le visible vers 550 nm. Les intensités de ces bandes sont nettement plus élevées que celles des ions libres B^{2-} et C^{2-}.

Ces résultats concordent pour indiquer que la substitution des hydroxyquinones par le brome ou par le chlore n'a pratiquement pas d'influence sur les transitions électroniques, dans les complexes comme dans les ions. Nous pensons que ce résultat est dû à la délocalisation des charges dans les ligands et dans les ions, qui "amortit" l'effet attracteur des substituants. La preuve en est que les spectres des acides (et dans une moindre mesure ceux des ions HB^- et

Tableau 2. Spectres électroniques de H_2B, de ses ions et des complexes de W(VI)

Espèce	Ultraviolet λ, nm	Ultraviolet ϵ, $l.mol^{-1}.cm^{-1}$	Visible λ, nm	Visible ϵ, $l.mole^{-1}.cm^{-1}$
H_2B	311,5	$1{,}80.10^4$	455	230
HB^-	315	$1{,}60.10^4$	522,5	870
B^{2-}	334	$2{,}65.10^4$	520	190
complexe 1:2	335	$2{,}25 \pm 0{,}05^*.10^4$	550	$450 \pm 50^*$
complexe 1:1	334	$1{,}80.10^4$	550	900

* Incertitude due au complexe 1:1 qui se forme simultanément.

Tableau 3. Spectres électroniques de H_2C, de ses ions et des complexes de W(VI)

Espèce	Ultraviolet λ, nm	Ultraviolet ϵ, $l.mole^{-1}.cm^{-1}$	Visible λ, nm	Visible ϵ, $l.mole^{-1}.cm^{-1}$
H_2C	302	$2{,}04.10^4$	460	200
HC^-	310	$1{,}63.10^4$	530	870
C^{2-}	332	$2{,}72.10^4$	525	190
complexe 1:2	333	$2{,}35 \pm 0{,}05^*.10^4$	555	$450 \pm 50^*$
complexe 1:1	331	$1{,}80.10^4$	550	870

* Incertitude due au complexe 1:1 qui se forme simultanément.

HC^-), dans lesquels il n'y a pas délocalisation, diffèrent assez sensiblement.

D'autre part, les bandes d'absorption des différents complexes varient peu avec la nature du cation. Dans le cas de l'acide chloranilique, très étudié, les complexes de U(VI),[9] Zr(IV),[10] Hf(IV)[11] et Nb(V)[12] présentent un maximum d'absorbance dans l'ultra-violet entre 330 et 340 nm. Ce résultat, vérifié aussi dans le cas de l'acide bromanilique,[3] confirme que le ligand a pratiquement la même structure électronique dans tous ces complexes. Là aussi, le rôle de la délocalisation électronique paraît déterminant.

Dosage du tungstène(VI) en milieu perchlorique 1,4M

Nous avons déterminé les conditions optimales pour doser W(VI) par spectrophotométrie en utilisant la formation des complexes 1:1 en milieu très acide. Nous avons choisi une molarité d'acide égale à 1,4*M*, afin de comparer directement le dosage de W(VI) à celui de Mo(VI) étudié précédemment.[3]

Pour chaque réactif, la longueur d'onde retenue est celle qui correspond à la plus grande différence d'absorbance entre l'acide libre et le complexe.

Résultats. Nous avons mesuré l'absorbance de deux solutions de H_2B et H_2C $10^{-3}M$ en fonction de l'addition de W(VI), le diacide étant en excès. Les graphes $A = f([W(VI)]_T)$ sont des droites dans le domaine de concentration utilisé.

Elles ont pour équations:

H_2B $\quad A = 0{,}530 + 1{,}56.10^4\,[W(VI)_T]$ à $\lambda = 340$ nm

H_2C $\quad A = 0{,}300 + 1{,}30.10^4\,[W(VI)_T]$ à $\lambda = 340$ nm

$\quad A = 0{,}440 + 1{,}48.10^4\,[W(VI)_T]$ à $\lambda = 335$ nm

On a calculé α à partir de la relation $p = \epsilon_X l\alpha$ où p est la pente de la droite, ϵ_X est l'absorbance molaire du complexe, l est la longueur du trajet optique, α est la proportion de W(VI) complexé.

Nous avons montré ci-dessus que le même complexe 1:1 était formé du milieu $HClO_4$ 1*M* à pH 2. Les absorbances ϵ_X des deux complexes de B^{2-} et C^{2-} ont donc été déterminées par lecture directe à pH 2,10 en présence d'un excès de W(VI) ($q = 2{,}0$).

Les résultats pour ϵ_X, α et K_f sont regroupés dans le tableau 4. Comme dans l'article précédent,[3] K_f se calcule par la relation:

$$K_f = \frac{\alpha}{1-\alpha} \cdot \frac{1}{[\text{acide}]_T}$$

Puisque α est proche de l'unité pour les deux ligands, la proportion de W(VI) libre est toujours faible à l'équilibre et on peut considérer que la polymérisation du tungstène est négligeable. Ceci nous autorise à calculer les constantes conditionnelles de formation des deux complexes en admettant que le tungstène(VI) libre se trouve à l'état monomère.

Discussion. Pour le dosage du tungstène(VI) en milieu perchlorique 1,4*M*, l'acide bromanilique est plus sensible que l'acide chloranilique, puisque la pente de la droite de Beer est plus forte. Il faut noter que la longueur d'onde donnant les résultats les meilleurs n'est pas la même pour les deux ligands ($\lambda = 340$ nm pour H_2B et 335 pour H_2C). Ce phénomène n'était pas observé au cours du dosage du molybdène(VI) dans le même milieu,[3] et est dû à l'allure différente des spectres dans l'ultra-violet des deux complexes de W(VI).

On peut préciser la sensibilité du dosage en calculant la concentration de W(VI) qui provoque un accroissement de l'absorbance égal à 0,1 ($l = 1{,}00$ cm):

$-6{,}41.10^{-6}M$ (ou 1,18 mg/l.) pour H_2B $10^{-3}M$, $\lambda = 340$ nm,

$-6{,}76.10^{-6}M$ (ou 1,24 mg/l.) pour H_2C $10^{-3}M$, $\lambda = 335$ nm.

Le rapport des K_f des complexes tungstiques est:

$$\frac{K_f(H_2B)}{K_f(H_2C)} = 1{,}70$$

Cette valeur est pratiquement identique à celle (1,62) trouvée dans le cas des complexes molybdiques. Rappelons qu'elle correspond au rapport des valeurs de K_1 (première constante d'ionisation) des deux acides. Notre interprétation antérieure se trouve ainsi confirmée et étendue: les ions HB^- et HC^- présentent la même affinité vis-à-vis des ions de Mo(VI) et de W(VI).

La plus grande facilité de formation des complexes de H_2B s'explique par la plus grande acidité de ce réactif. Le masquage de l'ion HB^- par les protons se produit à des acidités supérieures à celles nécessaires pour masquer HC^-.

Le pourcentage de complexation des deux ligands est plus fort pour W(VI), comme le montre le tableau 5, où l'on compare les K_f des différents complexes.

Pour les deux ligands, le rapport de sélectivité est sensiblement le même, ce qui s'explique par la nature

Tableau 4. Calcul de K_f pour les complexes tungstiques de H_2B et H_2C dans $HClO_4$ 1,4*M*

Acide	λ, nm	ϵ_X, $l.mole^{-1}$ cm^{-1}	p, $l.mole^{-1}$	α	K_f
H_2B	340	$1{,}65.10^4$	$1{,}56.10^4$	$0{,}94_5$	$1{,}72.10^4$
H_2C	335	$1{,}62.10^4$	$1{,}48.10^4$	0,91	$1{,}01.10^4$
	340	$1{,}42.10^4$	$1{,}30.10^4$		

$[\text{acide}]_T = 10^{-3}M$; $l = 1{,}00$ cm; $T = 298$ K.

Tableau 5. Comparaison des K_f des complexes de Mo(VI) et W(VI)

	K_f		$\frac{K_f(W)}{K_f(Mo)}$
	Mo(VI)	W(VI)	
H_2B	$2{,}85.10^3$	$1{,}72.10^4$	6,04
H_2C	$1{,}78.10^3$	$1{,}01.10^4$	5,67

$[acide]_T = 10^{-3}M$; $T = 298$ K; milieu $HClO_4$ 1,4*M*.

très voisine des ligands. La présence d'atomes Cl ou Br ne semble pas avoir d'influence mesurable.

Dosage d'échantillons contenant du tungstène: interférences. La méthode s'applique au dosage des solutions contenant du tungstène(VI) en présence d'ions métalliques bivalents ou tervalents. En effet, ceux-ci sont précipités lors du traitement en milieu alcalin, cette opération étant nécessaire pour détruire les isopolyanions de W(VI) éventuellement présents dans la solution. Si une extraction préalable est nécessaire, on peut choisir une de celles citées dans la référence 19. Les ions gênants sont les mêmes que ceux intervenant dans le dosage du molybdène: Zr(IV), Hf(IV), U(VI), Cr(VI), V(V) [et naturellement Mo(VI) lui-même].

Etude des complexes solides des ions B^{2-} et C^{2-}

Préparation et formule. Il aurait été souhaitable de précipiter les complexes de W(VI) et Mo(VI) caractérisés en solution aqueuse, mais leur trop grande solubilité ne l'a pas permis. Aussi, après avoir vérifié que les complexes 1:1 se formaient également dans le méthanol pur, nous avons isolé des composés solides par évaporation de ce solvant. Les produits ont été purifiés par lavage à l'acétone, dans laquelle ils sont insolubles, afin d'éliminer l'excès de H_2C et H_2B.

L'analyse indique les formules suivantes:

—complexes tungstiques:

$$WO_3,\ C_6O_4Br_2,\ 2Na,\ 4H_2O$$
$$WO_3,\ C_6O_4Cl_2,\ 2Na,\ 3H_2O.$$

Le complexe bromanilique s'hydrate progressivement de $3H_2O$ à $4H_2O$ en fonction du temps.

—complexes molybdiques:

$$MoO_3,\ C_6O_4Br_2,\ 2Na,\ 3H_2O.$$

D'autres mesures ont indiqué $2H_2O$, mais là encore, l'hygroscopicité du produit a été mise en évidence.

$$MoO_3,\ C_6O_4Cl_2,\ 2Na,\ 3H_2O$$

(étudié antérieurement[2]).

Les composés tungstiques 1:2 n'ont pas pu être obtenus par cette méthode, probablement parce que le pH optimum de leur formation n'est pas atteint. Les essais d'évaporation d'un mélange tungstate de sodium 1:2 acide chloranilique dans le méthanol ont conduit à un mélange solide de complexe 1:1 et de H_2C (identifié en infra-rouge).

Spectres dans l'infra-rouge des complexes. Les spectres des complexes solides ont été enregistrés entre 4000 et 200 cm^{-1}, après dilution dans des pastilles de bromure de potassium. On sépare aisément les bandes dues au ligand coordonné et celles dues au groupement inorganique.

Nous ne considèrerons ci-dessous que les bandes les plus intenses, dont l'attribution est indiscutable et permet de préciser la nature des liaisons entre atomes. Nous avons mis en évidence l'influence du cation sur le ligand en enregistrant dans les mêmes conditions les spectres de H_2B, de deux de ses sels (K et Ca) et de deux de ses chélates (Zn et Cu).

Bandes dues au ligand bromanilate. Le tableau 6 regroupe les nombres d'onde des bandes attribuées aux vibrations ν_{O-H}, $\nu_{C=O}$, ν_{C-O} et ν_{C-Br} dans les composés bromaniliques.

Toutes les bandes ci-dessus sont d'intensité forte ou très forte. La vibration ν_{C-Br} est parfois moyenne.

Les résultats pour CuB et ZnB sont très proches de ceux décrits par Bottei.[7] L'intervention des groupes OH et CO dans la complexation de H_2B est attestée par la disparition de la vibration de valence ν_{O-H} et le déplacement des vibrations de valence ν_{C-O} et $\nu_{C=O}$. Seuls, les complexes hydratés présentent un pic intense vers 3500 cm^{-1}.

Le spectre de K_2B est très simple et correspond vraisemblablement à celui de l'ion aromatique B^{2-} dont la haute symétrie se traduit par une seule bande ($\nu = 1530$ cm^{-1}) pour la vibration carbone–oxygène, qui correspond alors à une liaison de multiplicité 1,5. Le même phénomène est observé pour le sel de calcium.

La diminution de $\nu_{C=O}$ pour les chélates de zinc et de cuivre montre que la liaison C=O y est très polarisée et tend vers la forme limite $>\overset{+}{C}-\bar{O}$. Au contraire, le nombre d'onde voisin de 1570 cm^{-1} pour les complexes de W(VI) et Mo(VI) indique que la liaison C=O a une multiplicité intermédiaire entre 2 et 1,5 dans ces deux composés.

Tableau 6. Nombres d'onde (en cm^{-1}) des vibrations dues à l'ion bromanilate salifié ou complexé

Composés	H_2B	complexe Mo(VI)	complexe W(VI)	K_2B	CaB	ZnB	CuB
ν_{O-H}	3230	3490	3470	—	3480	3450	—
$\nu_{C=O}$	1655 1620*	1575	1565	1530	1520	1515	1485
ν_{C-O}	1270	1375	1375	—	1380	1380	1360
ν_{C-Br}	810 800	815	810	795	810	835	825

* La bande la plus intense.

La vibration de valence ν_{C-O} est observée pour tous les sels et complexes vers 1370 cm^{-1} et ne semble pas varier avec la nature du cation. Enfin, la vibration ν_{C-Br} est peu affectée par la complexation.

Bandes dues au ligand chloranilate. Le spectre du ligand C^{2-} dans le complexe tungstique est pratiquement identique (à 10 cm^{-1} près) à celui observé dans le cas du complexe molybdique.[2] Les nombres d'onde sont 3500 cm^{-1} (ν_{OH}), 1565 cm^{-1} ($\nu_{C=O}$), 1380 cm^{-1} (ν_{C-O}) et 845 cm^{-1} (ν_{C-Cl}).

On observe la même évolution de $\nu_{C=O}$ avec la nature du cation, le nombre d'onde décroissant selon la séquence:

$$H > Mo, W > K, Ca > Zn, Cu.$$

Bandes dues aux cations tungstiques. Les spectres des complexes de H_2B et H_2C présentent trois bandes caractéristiques du groupement inorganique. Deux bandes fortes situées à 930 et 885 cm^{-1} (H_2B) et à 935 et 885 cm^{-1} (H_2C) ont été attribuées aux vibrations de valence W=O symétrique et antisymétrique.[13] Ce doublet est caractéristique d'un arrangement cis des deux atomes d'oxygène dans l'entourage octaèdrique de l'atome de tungstène.

Une bande large et forte située à 630 cm^{-1} (H_2B) et 635 cm^{-1} (H_2C) indique la présence de ponts W–O–W.[14] Nous en concluons que le solide a une structure condensée.

Bandes dues aux cations molybdiques. Alors que le complexe chloranilique de Mo(VI) présente un spectre dans l'infra-rouge analogue à celui du complexe tungstique (doublet caractéristique[13,15,16] d'un groupement MoO_2 *cis*), le composé bromanilique est anormal. On n'observe en effet qu'une seule bande pour la vibration de valence Mo=O (ν = 890 cm^{-1}). La finesse de cette bande exclut toute confusion avec le doublet attendu (ν = 925 et 880 cm^{-1} pour le complexe chloranilique).

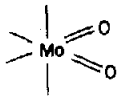
Les deux complexes molybdiques présentent une bande large et forte à 740 cm^{-1} (H_2B) et 750 cm^{-1} (H_2C) qui caractérise les ponts Mo–O–Mo.[14] Ils sont donc condensés à l'état solide.

Discussion

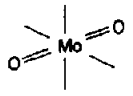
Complexe molybdique de H_2B. La présence d'une bande unique, étroite et très intense à 890 cm^{-1} constitue, à notre connaissance, un phénomène qui n'a jamais été observé auparavant dans les composés du molybdène (VI).

Après avoir vérifié que le molybdène avait effectivement le degré d'oxydation VI dans le complexe, il ne reste que deux interprétations possibles pour l'unicité de la bande.

(*a*) Le groupement molybdique aurait la structure *trans* MoO_2. Cependant, tous les composés du dioxomolybdène(VI) connus à l'heure actuelle présentent la configuration *cis*. D'autre part, la non-existence de composés *trans* a été justifiée par des arguments théoriques[13] qui s'accordent avec tous les résultats expérimentaux obtenus avec différents ions métalliques.



structure *cis*



structure *trans*.

(*b*) Le groupement molybdique ne comporterait qu'un seul atome d'oxygène lié au molybdène. Bien qu'une telle structure n'ait jamais été observée jusqu'à présent, elle ne semble pas en désaccord avec les théories généralement admises.

En conclusion, le complexe bromanilique de Mo(VI) ne contient pas de groupements dioxomolybdène *cis*. Une détermination de structure serait souhaitable, mais la grande solubilité du complexe dans l'eau ne nous a pas permis d'isoler un monocristal jusqu'ici.

Aromaticité des ligands. Le déplacement de la vibration de valence $\nu_{C=O}$ des deux ligands avec la nature du cation coordonné nous paraît être un phénomène remarquable et qui a peu d'équivalents chez les complexes métalliques d'énols.

La littérature concernant les spectres dans l'infrarouge des chélates de l'acétylacétone et des oxalates a été discutée par Cotton,[17] qui a montré que les variations de fréquence de $\nu_{C=O}$ n'étaient pas proportionnelles à la stabilité des complexes. Par contre, une corrélation a été établie entre $\nu_{C=O}$ et les constantes de stabilité des complexes de l'aldéhyde salicylique.[18] Il faut noter que, dans ce composé, la liaison C=O n'est pas engagée dans un système résonnant, et peut donc être affectée directement par le cation métallique.

Dans le cas des ions B^{2-} et C^{2-}, les liaisons C=O participent à la délocalisation électronique, et on observe en effet des variations faibles de $\nu_{C=O}$ en fonction de la nature des cations divalents, qui ne sont pas reliées à la stabilité des complexes.[7] Par contre, dans les complexes de Mo(VI) et W(VI), $\nu_{C=O}$ prend une valeur ($\simeq$1570 cm^{-1}) très différente de celle des acides ($\simeq$1620 cm^{-1}), des sels ($\simeq$1525 cm^{-1}) et des chélates ($\simeq$1500 cm^{-1}).

Les complexes des ions métalliques de la colonne VIB constituent donc une famille de composés qui se différencient nettement des sels et des chélates de B^{2-} et C^{2-}. Rappelons qu'ils s'en différencient également par leur grande solubilité dans l'eau.

CONCLUSION

L'acide chloranilique et l'acide bromanilique permettent le dosage spectrophotométrique du tungstène(VI) en milieu $HClO_4$ 1,4*M*. A notre connaissance, il s'agit d'une des rares méthodes de dosage du tungstène n'exigeant pas de réduction préalable.[19] Nous avons précisé les conditions opératoires et la sensibilité de ces dosages, pour lesquels la principale interférence provient du molybdène(VI).[2,3]

Le calcul des constantes conditionnelles de formation des deux complexes 1:1 formés par W(VI) avec les ions B^{2-} et C^{2-} montre que les complexes tungstiques sont plus stables que les complexes molybdiques correspondants. Nous avons constaté aussi que les meilleurs résultats obtenus avec H_2B sont dus à la plus grande acidité de ce réactif.

L'étude des solides 1:1 formés entre Mo(VI), W(VI) et les dihydroxyquinones a permis de mettre en évidence le caractère particulier des composés formés avec les ions hydrolysés en milieu acide. Ceux-ci ne donnent pas de polymères de coordination comme les métaux divalents, mais des complexes solubles qui peuvent recevoir des applications analytiques. La différence de propriétés provient vraisemblablement de la différence de caractère covalent des liaisons métal–oxygène que nous avons détectée dans le spectre infra-rouge.

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Summary—The complexes formed from tungsten(VI) and chloranilate (C^{2-}) and bromanilate (B^{2-}) have been studied in aqueous solution and as solids, by ultraviolet, visible and infrared spectroscopy. At pH 3–4, the complexes have the composition ligand:tungsten = 2. At pH < 2, only the 1:1 complexes are found. The two reagents allow the spectrophotometric determination of W(VI) (λ = 335 nm for H_2C and 340 nm for H_2B) in 1.4*M* $HClO_4$, at concentrations of about 1 mg/l. The conditional stability constants of the two 1:1 complexes in this medium have been calculated. The tungsten complexes are more stable than the corresponding molybdenum complexes, and the complexes of B^{2-} are more stable than the complexes of C^{2-} [with W(VI) and Mo(VI)]. It is shown that this result is due to the difference between the pK_1 values of the acids H_2B and H_2C. The infrared spectra of the complexes of B^{2-} and C^{2-} with Mo(VI) and W(VI) are discussed in order to define the interaction between the metal ions and the ligands.

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GRAPHITE FURNACE AND FLAME ATOMIC-ABSORPTION TECHNIQUE FOR THERMOANALYTICAL INVESTIGATIONS*

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Summary—Aerosol particles formed from the vapour of electrothermally heated substances were introduced into an acetylene–air flame for atomization and detection. Thus individual observations could be made on condensed phase processes taking place in the furnace. Curves of absorbance *vs.* furnace temperature for several zinc compounds were recorded and compared with the corresponding thermoanalytical DTG-curves.

The electrothermally heated graphite or metal atomizers are known to give the highest absolute detection power in atomic spectrometry. It has also been recognized that controlled electrothermal heating offers new possibilities for following high-temperature reactions and thus making progress in basic knowledge of spectrochemistry. Besides elucidation of chemical interferences and selection of optimum analytical conditions, the method can yield thermochemical data in general. One of the problems in this context seems to be that condensed-phase and gas-phase reactions take place simultaneously in the furnace, both resulting in the formation of free atoms. Therefore the "appearance temperature" corresponding to limiting detection of atomic absorption may differ appreciably from the temperature corresponding to formation of a volatile species. This might be one of the reasons why the conclusions of different authors are contradictory in regard to atomization mechanisms. Campbell and Ottaway[1] concluded that the atomization temperature of Al_2O_3, CdO, Mn_3O_4 and ZnO is governed by reduction by carbon in the solid phase, whereas according to Sturgeon *et al.*[2] their dissociation in the gas phase is the dominant factor.

The combined technique described here may permit more accurate determination of the initial temperature of vaporization, resulting in further experimental evidence on the mechanism of atomization. In addition, following high-temperature decomposition processes in the condensed phase overlaps with the aims of thermoanalytical methods. With the spectroscopic method the derivative of the weight loss caused by vaporization of metal-containing species can be followed, which corresponds in principle to a differential thermogravimetriic (DTG) curve.

* Presented in part at EUROANALYSIS III, Dublin, 1978.

EXPERIMENTAL

Apparatus

The graphite furnace and flame photometer combination based on a Varian Techtron Model CRA 63 system has been proposed previously for solid-sample analysis[3,4] and its improved version is shown in Fig. 1. An injector is used to suck the aerosol into the mixing chamber of an atomic-absorption flame spectrophotometer (Pye Unicam Model SP 90A in this work) and thus no gas-tight enclosure to the furnace is needed. The double-chamber system shown can be used with an acetylene–air flame with air flowing laterally into the upper chamber as well, increasing the flow-rate through the aerosol transport system. When the acetylene–nitrous oxide flame is used, only the upper chamber is used and its bottom edge rests on the sheath-gas duct of the furnace. In that case the suction rate and the flow-rate of the sheath gas should be equalized. The length of the connecting plastic tube is about 30 cm. The smaller the volume of the mixing chamber the less the transit time of the aerosol, this being important in this work. With the mixing chamber of the basic instrument the transit time was 1.2 sec at the flow-rates suitable for a stoichiometric acetylene–air flame (acetylene 1.8 l./min). To shorten this time the original mixing chamber was replaced with a plastic T-junction, and a transit time

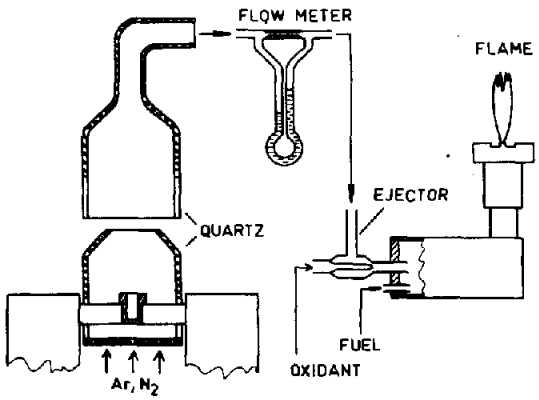

Fig. 1. Schematic diagram of the graphite furnace–flame combination.

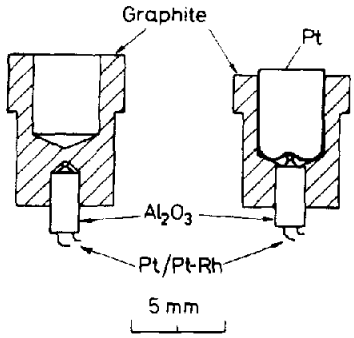

Fig. 2. Shape of the graphite cups with and without a platinum crucible, and the mount of the thermocouple. Cups were coated with Pyrolyticgraphite.

of 0.63 sec was attained. Details of an efficient and easily fabricated injector have been described elsewhere.[5] The optimum conditions for an ordinary acetylene–air single-slot (10 cm) burner were used. The flow-rate of the argon sheath gas in the furnace was 3 l./min.

The power source of the furnace was used in the ramp and its minimum ramp-rate mode adjusted to 0.028 V/sec by an electrical modification. This ramp-rate ensured a heating rate less than 10°/sec below 400°, increasing linearly with temperature up to 32°/sec (1250°), when the graphite cups shown in Fig. 2 were used. The technique of holding and fixing the thermocouple was taken from thermoanalytical practice. In the graphite cup on the left, a 1-mm wall thickness separates the sample (bottom) and the measuring junction, which might be too large if indirect heating were the effective means of heat transfer. However, with this system the heating current flows through the wall and we can suppose that the temperature is approximately the same on both sides of it. The wall thickness of the platinum crucible placed in the graphite cup shown on the right was 0.05 mm, ensuring appropriate heat transfer. Besides a Pt/Pt–Rh thermocouple (max. 1650°), a chromel/alumel thermocouple (max. 1200°) was also applied in certain cases; it fits the Dupont Thermal Analyser Model 990 for direct readings on a calibrated temperature scale. The comparative measurements on zinc compounds were made with this apparatus and its *X–Y–Y'* recorder was used for the spectroscopic measurements as well.

Procedure

Stock solutions of the elements studied were prepared and portions were diluted to the concentration levels suitable for measurements with 1-μl sample volumes (see corresponding figures). This small sample volume, applied as nearly as possible on the same spot in the cup, was advantageous in increasing reproducibility and it made the application of a previous drying stage unnecessary. Matrix materials and acid were added in the same 1-μl volume when desired, *i.e.*, they were not applied separately. Only traces of zinc metal powder were used as the solid for spectroscopie studies. For comparative measurements with the thermoanalytical instrument, 5–10 mg of solid sample, a platinum crucible, argon atmosphere and heating rate of 10 /min were used.

RESULTS AND DISCUSSION

Accuracy of temperature measurements

In the combined system the absorption signal of the species evolved has a delay relative to the thermocouple signal, which causes a positive error in the determination of characteristic points. As mentioned above, this delay was minimized, and with the heating rate used a maximum positive error of 10–20° could be expected. However, there may also be sources of negative error, the major one probably being the cooling effect of the twin alumina tube (Fig. 2) at the relatively high heating rate. Problems of heat transfer to the sample and heat conductivity inside the sample are probably not encountered with sample weights less than 1 μg. The various sources of error with opposite sign could result in error compensation, so no temperature correction was made.

The error can be estimated quantitatively from comparative measurements discussed later and a semi-quantitative approach is demonstrated in Fig. 3. Sodium emission curves for low amounts of sodium chloride (100–300 ng of sodium) and the heating curves with higher amounts (3 mg of sodium chloride) are also shown. The slot-burner head was aligned perpendicularly to the direction of observation to decrease self-absorption, thus no perceptible difference from the corresponding atomic-absorption curves was found. The heating curves (A, B, C) were recorded with a higher amount of sample (not introduced into the flame) to observe the temperature delay due to the melting and boiling of the substance. The jumps on the curves close to the melting and boiling points of sodium chloride show a 20–30° positive deviation from the literature values. However, this error may be due to the larger amount of sample used and it is unlikely to be encountered with the spectroscopic measurements.

These studies were repeated with a graphite cup and no essential difference was found for the emission curves. However, the temperature delays on the heating curves with larger amounts of sodium chloride

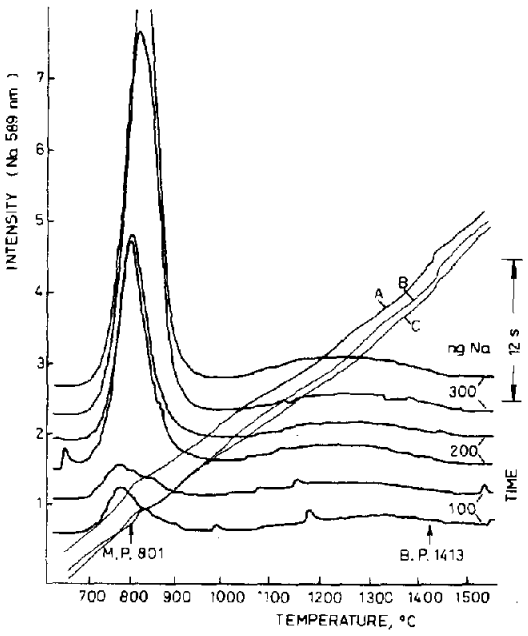

Fig. 3. Sodium emission *vs.* furnace temperature (100, 200, 300 ng of Na as NaCl solution) and heating curves (A, B, C) of 3 mg of NaCl in a platinum crucible.

could not be detected because of the thicker wall of the cup.

According to the emission curves in Fig. 3, most of the micro-amount of sodium chloride is evaporated at the melting point, but a small fraction is evolved at temperatures near the boiling point. The latter phenomenon may be due to a high-temperature process on the platinum surface, a matter for future investigation.

Characteristic temperatures

The emission peaks in Fig. 3 show a relatively small shift towards higher temperature with increasing amounts of sodium chloride (the small peaks due to the entrained dust particles should be ignored). In contrast the initial points of the sodium signal seem to occur at the same temperature (650°), although the initial curvature can be seen more clearly with the higher amounts. Similar characteristics were found by others[2] using a graphite tube atomizer, and are also observed in thermoanalytical practice (dynamic heating). From these and related works[6] it can be concluded that the heating rate affects primarily the shape and position of the peaks, but this has not been studied with the system in question.

With silver nitrate it was found that the amount of sample has a strong influence on the temperature at which the absorbance peak appears but no effect on the initial appearance temperature (Fig. 4). This compound decomposes at 444° to give the metal, which melts at 960.8°.[7] The initial point of the sublimation occurs at 870° in Fig. 4 and it can be assumed that small isolated silver grains are involved in this process. However, with larger amounts of sample, a substantial number of silver grains form globules and the maximum rate of vaporization appears at higher temperature. In contrast to the case of silver, the absorbance *vs.* temperature curves of zinc nitrate in the graphite cup (Fig. 5) show no effect of sample weight on the position of the peaks. As discussed later, a reaction with the graphite cup was expected, with formation of gaseous products, a significant difference from the case of silver. Nevertheless, in agreement with the authors quoted it can be concluded that the initial (or appearance) temperatures can be considered as characteristic of substances and processes, being less affected by other parameters.

Calculation of the heat of vaporization of sodium chloride, silver and zinc (as metal powder) was attempted, based on the assumptions and theory adopted for a graphite tube atomizer.[2] The toe portion of the absorbance *vs.* temperature curves (referred to as A–T curves in the following) was used similarly and the log A values were plotted against $1/T$ where T is the absolute temperature. Although these plots were linear at low absorbances, the heats calculated from the slopes deviated appreciably from the literature values (lower with sodium chloride, higher with silver and zinc). However, if a lower heating rate was used close to the appearance of the signal ("ash" stage of the power source) fairly good agreement was found for silver.

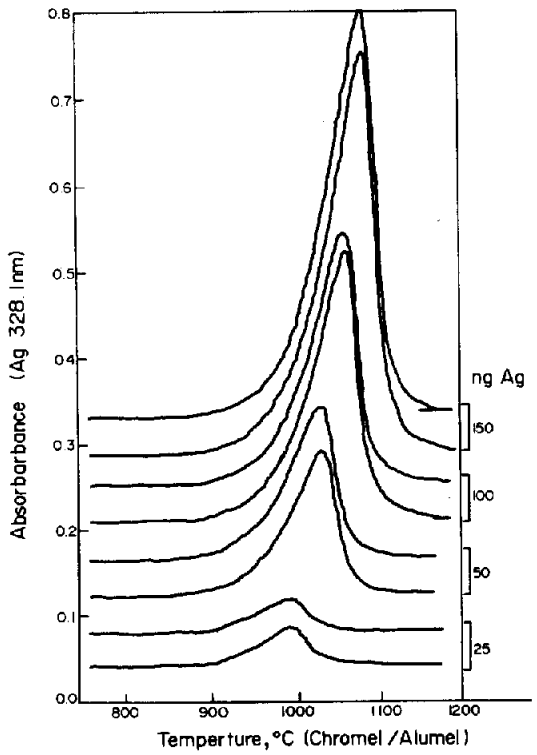

Fig. 4. Silver absorbance *vs.* furnace temperature (25, 50, 100, 150 ng of Ag as $AgNO_3$ solution in a graphite cup).

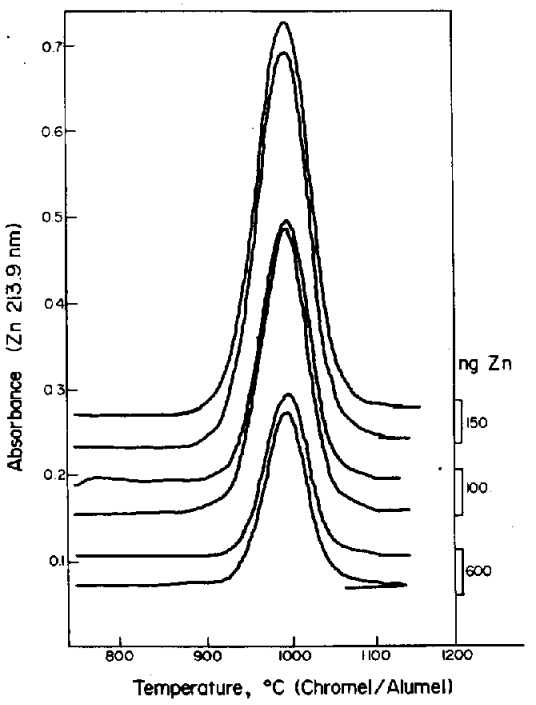

Fig. 5. Zinc absorbance *vs.* furnace temperature [60, 100, 150 ng of Zn as $Zn(NO_3)_2$ solution in a graphite cup].

Investigation of zinc and zinc compounds

Zinc metal. About 10 μg of powder was applied to the graphite cup and the initial temperature of vaporization was found to be 500°. This temperature is higher than expected, because zinc melts at 423° and has a vapour pressure of 1.4 mmHg at 500°.[7] Perhaps the presence of graphite plays some role in this respect, which will be the subject of further studies. Use of a platinum crucible should be avoided because of possible alloy formation.

Zinc nitrate. The sample, in dilute (pH ~ 4) nitric acid, was placed in the graphite cup, and from the corresponding A–T curves in Fig. 5, an initial temperature of 870° can be estimated for the evolution of zinc. Similar measurements with a platinum crucible and a Pt/Pt–Rh thermocouple resulted in a single initial point in the 1320–1400° range, as can be seen in Figs. 7 and 8 (for zinc chloride, discussed later).

Thermogravimetric (TG and DTG) curves for $Zn(NO_3)_2.6H_2O$ showed that there was complete decomposition to ZnO at 290° and no further change up to 1200°. A stoichiometric mixture of ZnO (87%) and graphite powder (13%) resulted in an initial definite weight loss at 810°. With two separate layers of these substances, one placed on top of the other, the corresponding temperature was 840° but a small gradual loss of weight started at around 700°.

The Gibbs free energy for the reaction of $ZnO_{(s)}$ and $C_{(s)}$ becomes zero at 953, 927 and 900°, depending on whether the product is $Zn_{(g)}$, $Zn_{(l)}$ or $Zn_{(s)}$ respectively.[1,2] The high vapour pressure of zinc at the reaction temperature (416 mmHg at 850°)[7] suggests that no equilibrium with the solid or liquid product exists. The appearance temperatures found with graphite atomizers[1,2] were 827° and 867°, in good agreement with the initial temperatures above and it may be concluded that carbon reduction in the solid phase plays a dominant role in the atomization of ZnO in graphite furnaces.

Zinc chloride. Samples in dilute (pH ~ 4) hydrochloric acid medium, in the *graphite cup*, produced the same form of *A–T* curves as zinc nitrate (Fig. 5). This suggests that a low concentration of zinc chloride in a nearly neutral aqueous solution undergoes complete hydrolysis and zinc oxide is formed on heating and reacts with carbon (see above). In Fig. 6, *A–T* curves of zinc chloride in 6*M* hydrochloric acid solution are shown and exhibit significant differences. Two peaks are seen with initial temperatures of 340° and 960° for the highest concentration used. However, with decreasing amounts of sample the first initial temperature shifts to higher temperature (410°) and the second shifts to lower temperature (880°), the latter being less well defined. It can also be seen that the ratio of the lower to higher temperature peak heights decreases with the amount of sample.

The results obtained with a *platinum crucible* (Fig. 7 and in part Fig. 8) are important supplements to the findings above. As can be seen, the curve at the lower temperature splits into two peaks with increasing amount of zinc chloride and the peak at the lower temperature becomes dominant. This splitting shows itself apparently as a shift with the graphite cup (Fig. 6). With the platinum crucible no peak appears in the 880–960° range, indicating that this peak must be related to the presence of graphite. However, in the 1320–1400° range the start of another peak is observed, which is not the case with the graphite cup.

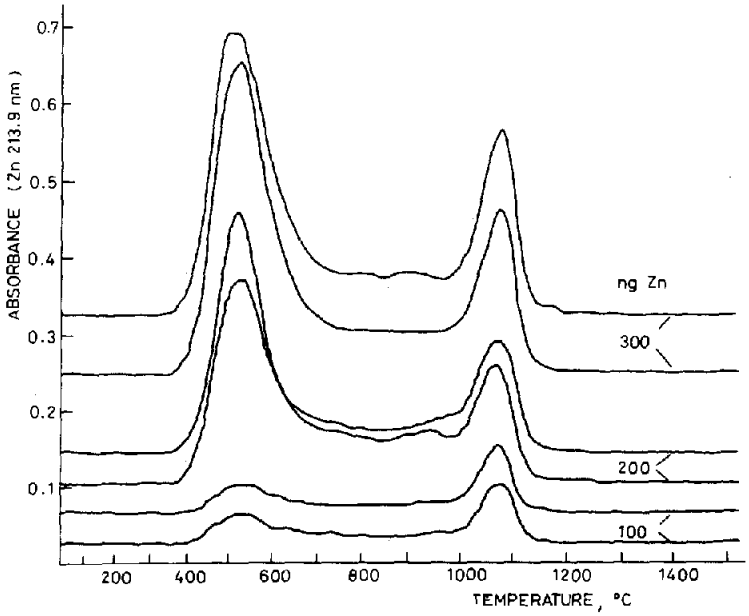

Fig. 6. Zinc absorbance *vs.* furnace temperature (100, 200, 300 ng of Zn as $ZnCl_2$/18% HCl solution, in a graphite cup).

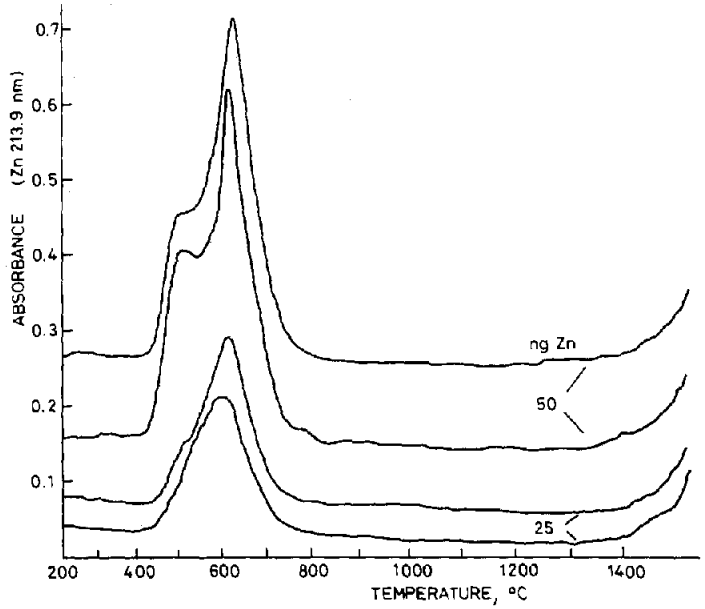

Fig. 7. Zinc absorbance *vs.* furnace temperature (25 and 50 ng of Zn as $ZnCl_2$/18% HCl solution in a platinum crucible).

The thermogravimetric curve of commercial zinc chloride (*pro analysi* grade) showed a stepwise weight loss of 18% up to 250°, a major loss (70%) between 350° and 510° and 12% remaining stable up to 800°. According to the DTG curve the major loss takes place in two steps, and the overlapping peaks give an inflection point at 460°. In the absence of references to related thermoanalytical studies, the basic inorganic chemistry of the compounds[8,9] was used for interpretation of the results. Zinc chloride is highly hygroscopic and the weight loss in the 150–250° range may be due to the decomposition of zinc chloride hydrates (the 1, 1.5, 2.5, 3 and 4 hydrates are known). $ZnCl_2$ melts at 315° and the initial temperature at 340–350°C can be related to its vaporization which is completed by about 460° (see also the studies of zinc ammonium chloride below). The boiling point of $ZnCl_2$ is 732° and it has a vapour pressure of 2.8 mmHg at 460°.[7] Chlorohydroxy zinc acids, such as $H(ZnCl_2OH)$ and $H_2[ZnCl_2/OH)_2]$ are said to exist in concentrated solutions,[8] but the thermal properties of these compounds have not been

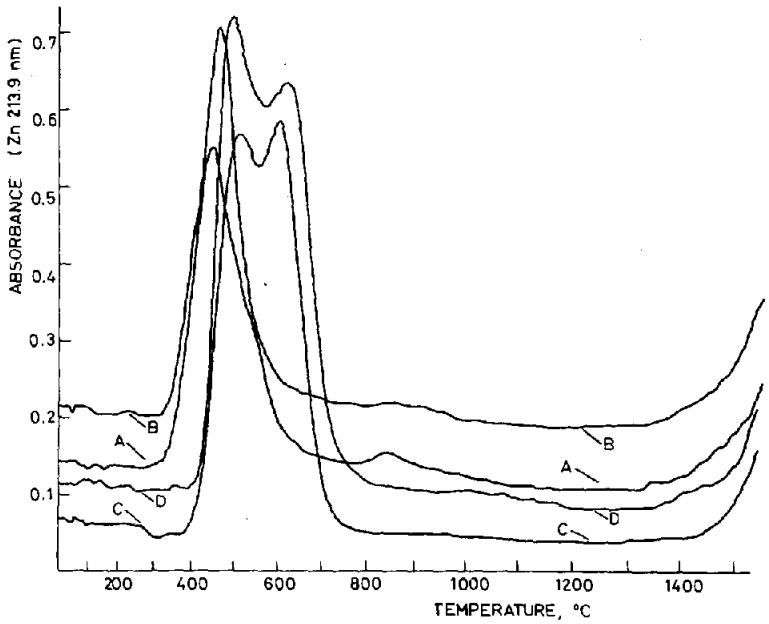

Fig. 8. Zinc absorbance *vs.* furnace temperature: (A, B) 100 ng of Zn as $ZnCl_2$/1% NH_4Cl solution, (C, D) 100 ng of Zn as $ZnCl_2$/18% HCl solution, in a platinum crucible.

reported. It is supposed here that the $ZnCl_2$ moiety of these compounds is released at a somewhat higher temperature range, 460–510°. A part of the water contained in the hydrated zinc chloride aids the decomposition to ZnO, which melts at 1980° but starts to sublime[8] at 1300°, in agreement with the findings in Figs. 7 and 8. In the graphite cup the remaining ZnO reacts with the supporting material in the 880–960° range at a very similar temperature to that for zinc nitrate (Fig. 5).

Studies of the atomization mechanisms of zinc chloride in hydrochloric acid media, with a graphite tube atomizer[2] showed an appearance temperature of 670 , which differs apprcciably from the vaporization points for both zinc chloride and zinc obtained by carbon reduction, shown in Fig. 6. During rapid heating (heating rate ~ 1000°/sec) zinc chloride vapours would not escape completely from the tube at up to 670° and their dissociation in the gas phase could be relevant to atomization, as concluded elsewhere.[2]

Molecular absorption measurements of zinc halides with a similar (mini-Massmann type) atomizer as in Fig. 1, and temperature measurements with a thermocouple,[10] are in some respects important supplements to the conclusions above. $ZnCl_2$ (applied in concentrated solution) started to evaporate in this form at 350° and a peak due to atomic absorption was recorded at higher temperature. Additions of hydrochloric acid and ammonium chloride to zinc nitrate resulted in a similar appearance of $ZnCl_2$ molecular absorption.

Zinc chloride with excess amounts of ammonium chloride in a platinum crucible gave the A–T curves (A, B) in Fig. 8, which may be compared with the curves obtained for excess of hydrochloric acid (C, D). With ammonium chloride, only one definite peak with an initial temperature of 300° was recorded and the start of a new peak was again seen in the 1320–1400° range. Corresponding recordings for use of the graphite cup showed very similar characteristics to the curves with hydrochloric acid (Fig. 6), including no shift of the first initial temperature from 350° to 300°, as is evident in Fig. 8 for use of a platinum crucible.

TG curves of the residues from solutions containing $ZnCl_2$ and NH_4Cl in stoichiometric ratio ($ZnCl_2 . 2NH_4Cl$) and excess of NH_4Cl, showed quantitative evolution of NH_4Cl up to 350°, a final evaporation stage between 350° and 460°, and 8–10% of the substance remaining stable up to 800°. DTG curves, for excess of NH_4Cl present, exhibited three peaks with initial temperatures of 150°, 250° (overlapped) and 350°, while without excess of NH_4Cl present only the last two could be observed. The decomposition in the range studied was complete at 460°, *i.e.*, no shift to 510° was found in contrast to the studies of zinc chloride above. From these results it is concluded that zinc does not vaporize in ammonium-bonded form under the conditions of the thermogravimetric measurements. The formation of $ZnCl_2 . 2NH_4Cl$ shifts the evolution of NH_4Cl to a higher temperature, but the double salt decomposes to $ZnCl_2$ which evaporates in the range noted. A small amount of ZnO was again formed as a final product, as found in the cases above.

However, the spectroscopic A–T curves in Fig. 8 indicate definitely that a more volatile zinc compound than zinc chloride was evolved under these special conditions. It is supposed that this compound is $ZnCl_2 . 2NH_4Cl$ which has melting and sublimation points[9] of 150° and 341° respectively. This assumption seems at least a reasonable hypothesis for future consideration.

Simultaneous measurements in the furnace and in the flame

The information gained by direct measurements in the furnace is of considerable importance from the point of view of graphite furnace spectrometry and the combined technique is intended to supplement (not to replace) these studies. However, sequential recordings with the atomizer and with the combined system suffer from the limitations of reproducibility of sample addition and clamping of the cup, particularly with the type of furnace used. This is more pronounced if absorbance *vs.* time (not temperature) recordings, which are useful enough for many practical purposes, are made directly. These uncertainties could be decreased by electronic signal averaging.[11]

Another possibility of improving the information content would be to operate two atomic-absorption spectrophotometers simultaneously, one of them arranged conventionally with the graphite atomizer and the other with a suitable flame into which the aerosol from the furnace is introduced.[12] As a preliminary to more detailed studies,[12] and as a demonstration only, this double spectrometric system has been used to study the effect of a sodium chloride matrix on the atomization of zinc nitrate.

The experimental conditions described above were used, with some modifications as follows. The CRA 63 was operated according to the manufacturer's recommendation in a Varian Techtron Model AA6 spectrophotometer, with the minimum ramp-rate for the unmodified power source, and commercial graphite cups. The other spectrophotometer was operated with its original (large volume) mixing chamber connected to the furnace with a 1.2-m long plastic tube. Both modifications increased the separation in time between the direct and indirect signals. A 5-μl sample was applied and dried, and to decrease the difference in magnitude between the direct and indirect signals, a less sensitive zinc line was used for the direct signals. Recordings were made with a fast X–Y–Y' recorder (Bryans, Model 26000 A3).

In Fig. 9, recorder traces of signals direct from the furnace (A_1,A_2), with deuterium-lamp background correction, and of signals from the furnace/flame combination (B_1, B_2) are shown. A_1 and B_1 were recorded simultaneously for matrix-free zinc nitrate and A_2 and

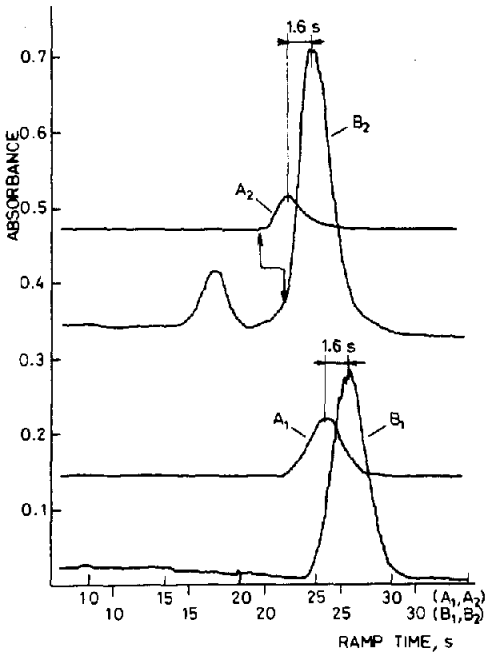

Fig. 9. Zinc absorbance in the furnace (A_1, A_2) and in the flame (B_1, B_2) monitored by two spectrophotometers as a function of ramp time. A_1 and B_1 were recorded simultaneously with 0.5 μg of Zn as Zn $(NO_3)_2$ solution and A_2, B_2 similarly in the presence of 130 μg of NaCl. For the furnace the Zn 307.6-nm line (corrected for background) and for the flame the Zn 213.9-nm line were used. The 1.6-sec shift of the time scale of curves B_1, B_2 corresponds to the time taken for the aerosol to reach the flame from the furnace.

B_2 for sodium chloride matrix also present. The difference between the time scales of the direct and indirect signals is clearly shown by the shift of the corresponding peaks (1.6 sec, marked) in agreement with calculations based on flow-rate and gas-volume measurements. The traces for zinc nitrate on its own show a single peak which can be related to that shown in Fig. 5. In the presence of sodium chloride some of the zinc evaporates at a lower temperature (presumably as $ZnCl_2$) and is monitored only by the flame. A shift of the vaporization of the main fraction of zinc to a lower temperature range is also obvious from the comparison of the B_1 and B_2 traces. It can also be seen that the toe portion of the larger peak of the B_2 trace is not monitored by the A_2 trace (marked with arrows), which means that gas-phase dissociation in the furnace is hindered at the corresponding temperature. The vaporization range of sodium chloride was found from separate studies to lie between the two peaks of the B_2 trace, overlapping mainly the second peak of zinc. Thus the reduction in the atomization temperature of zinc by sodium chloride might be related to co-evaporation as was concluded for the $PbCl_2$/NaCl system.[11]

Sample deposition, life-time of zinc vapours

In the transport system between the flame and the furnace, deposition of sample can usually be seen after long operation. Microscopic studies of a sodium chloride deposit showed that it consisted mainly of particles of 15–20 μm diameter. Experiments with cadmium nitrate in a similar transport system but with an arc-discharge as vaporizer[5] showed that 53% of the sample was introduced into the flame. The length of the tubing and the streaming parameters would be expected to affect the efficiency of transportation. A more important question is whether the chemical form of the species evolved has an influence on the transport efficiency. It can be answered by measuring integrated absorbances with different compounds of the analyte element.

It was found that the integrated zinc absorbance in the flame was significantly higher in the presence of hydrochloric acid and sodium chloride than that for zinc nitrate alone in a graphite cup (compare B_1 and B_2 in Fig. 9). On the other hand, without use of the fuel and the flame, a zinc atomic-absorption signal (corrected for light-scatter) could readily be measured in the absence of these matrices. This signal decreased in the presence of sodium chloride and disappeared with hydrochloric acid present. These results suggest that more analyte was lost when it entered the transport system in the form of metallic vapour. Studies on lead vapour under similar conditions[13] showed that it had a far shorter lifetime than that found by us for zinc. However, this example shows that the substance transported may be a vapour/aerosol mixture in certain cases.

The results gained so far for the different chemical forms of zinc reveal that the rate of entry of a certain species into the flame (Q_i) is proportional to the rate of evaporation of that species (Φ_i) in the furnace:

$$Q_i = \eta_i \Phi_i$$

where η_i is the transport efficiency of the species in question. The limitations of this proportionality and the parameters influencing η_i will be of major importance in future investigations.

CONCLUSIONS

The initial temperature of vaporization found with the spectroscopic method and with the conventional thermoanalytical method were in good agreement for the model substances selected for this comparison. Two conclusions are possible from these results. By the use of the graphite furnace–flame combination and a recording optical pyrometer the measuring range can be extended up to about 3000°, which offers new possibilities for thermoanalytical studies. In addition, the thermal behaviour of minor components and micro-samples can be investigated, which is not common with conventional techniques. Earlier research in this direction was attempted with an arc-emission technique.[14] Improvement of the graphite furnace–flame combination is possible by shortening the distance to be traversed by the vapour/aerosol mixture. However, from the results gained with the relatively

long transport system another important aspect becomes evident. This is the possibility of combining a flame atomic-absorption spectrophotometer with a conventional thermoanalytical apparatus having well established temperature programming and measurement conditions. This would not, however, be suitable for measurement of the absolute amount of substance evolved, but it would make it possible to follow the change of rate of evolution of metal-containing species, which might be useful for many purposes.

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VERGLEICH VERSCHIEDENER SPEKTROGRAPHISCHER ANALYSENVERFAHREN ZUR ANALYTISCHEN HOMOGENITÄTSPRÜFUNG AM BEISPIEL DER UNTERSUCHUNG VON KUPFERPROBEN

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Zusammenfassung—Für die analytische Homogenitätsprüfung mittels der destruktiven optischem Emissionsspektrographie wurden verschiedene Verfahren der näherungsweisen Ermittlung des Analysenfehlers miteinander verglichen, und zwar (1) Anfunkungen mehrerer räumlich eng benachbarter Probenstellen (2) Mehrfachanfunkungen ein und derselben Probenstelle, (3) örtliche Meßwertmittlung nach der Vielfleckmethode, (4) Zweilinienpaarverfahren nach Hemschik und Schuffenhauer und (5) das Dreilinienverfahren nach Skogerboe. Die genannten Verfahren wurden auf eine nickel- und cobaltdotierte Kupferprobe angewandt und die erhaltenen Aussagen untereinander und mit denen von Mikrosondenuntersuchungen verglichen.

Analytische Homogenitätsprüfungen erfolgen auf der Grundlage des *F*-Tests durch Vergleich der Streuung bei Messungen an unterschiedlichen Probenorten mit der Streuung bei Wiederholungsmessungen an ein und derselben Probenstelle.[1,2]

Während für zerstörungsfreie Analysenmethoden, wie z.B. die mit der Elektronenstrahlmikrosonde, die Ermittlung des Analysenfehlers unproblematisch ist,[3] sind für destruktive Verfahren wie die optische Emissionsspektralanalyse echte Wiederholungsmessungen am gleichen Probenort nicht möglich. Für spektrographische Homogenitätsprüfungen werden deshalb eine Reihe von Verfahren angewandt, mit deren Hilfe der Analysenfehler mehr oder weniger gut näherungsweise bestimmbar ist.

Durch Untersuchungen an ein und derselben Probe, einer Kupferscheibe von 40 mm Durchmesser, von der ungefähr 2/3 des Volumens mit Cobalt und Nickel zu je etwa 1 M – % dotiert war*, sollen verschiedene dieser emissionsspektrographischen Verfahren in ihren Homogenitätsaussagen miteinander verglichen werden.

Im einzelnen wurden folgende Verfahren der näherungsweisen Ermittlung des Analysenfehlers untersucht (Abb. 1).

(1) Anfunkungen mehrerer räumlich eng zusammenliegender Stellen in verschiedenen Probenbezirken.[4]

(2) Mehrfachanfunkungen ein und derselben Probenstelle in verschiedenen Probenbezirdken.[5]

(3) Örtliche Integration von Meßwerten nach der Vielfleckmethode.[6]

(4) Zweilinienpaarverfahren von Hemschik und Schuffenhauer.[7]

(5) Dreilinienverfahren nach Skogerboe.[8]

(6) Anfunkungen an undotierten Probenorten.

Die für alle Verfahren gleichen Anregungs- und Aufnahmebedingungen sind in Tabelle 1 zusammengestellt.

Bei den verglichenen Methoden wird von ganz unterschiedlichen Voraussetzungen ausgegangen, die es rechtfertigen, in der angegebenen Weise den Analysenfehler anzunähern. Bei den Verfahren (1) und (2) wird angenommen, daß sich in den eng benachbarten Gebieten die Zusammensetzung nicht oder nur unwesentlich ändert. Insbesondere bei Verfahren (1) ist die Erfüllung dieser Voraussetzung fragwürdig, da bei vier regelmäßig angeordneten Brennflecken des Durchmessers d die Homogenität in einen Probengebiet von $D = 2{,}5d$, bei drei regelmäßigen Flecken von $D = 2{,}25d$ angenommen werden *muß*. Bei den hier angewandten Versuchsbedingungen ist mit $D = 7{,}5$ bis 10 mm kaum mit einer Erfüllung der Prämisse zu rechnen.

Demgegenüber kann bei den relativ geringen Kratertiefen von 25 bis 60 μm, die mittels der angenwandten Hochspannungsfunkenanregung erhalten werden, weit ether Homogenität *in bezug* auf die untersuchte Gesamttiefe von 100 bis 250 μm vorausgesetzt werden, zumal das Aufschmelzen durch die jeweils vorangegangene Anfunkung zusätzlich homogenisierend wirkt. Bei isotropen Festkörpern verhalten sich die Wahrscheinlichkeiten dafür, daß die betrachteten Gebiete tatsächlich homogen sind, für die Verfahren (1) und (2) wie 1:50.

Bei Verfahren (3) wird eine örtliche Mittelwertbildung dadurch erreicht, daß jeweils n Probenstellen

* Diese Probe wurde uns freundlicherweise vom Mansfeldkombinat "Wilhelm Pieck", Forschungsinstitut für NE-Metalle DDR-92 Freiberg/Sa., zur Verfügung gestellt.

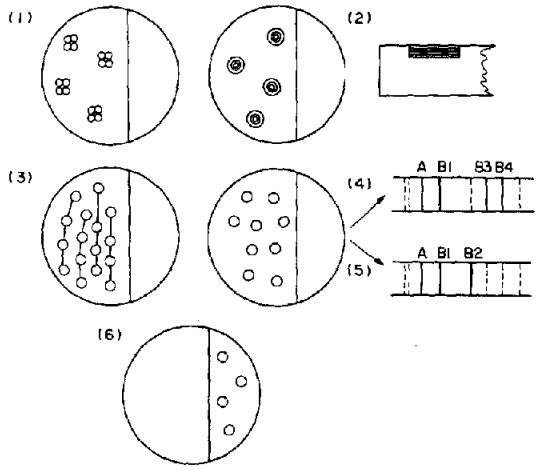

Abb. 1. Zur Veranschaulichung der Brennfleckanordnung auf der Probe; der rechte kleinere Teil ist undotiert. Die gleich großen Funkenflecken sind der Übersichtlichkeit halber unterschiedlich groß gezeichnet.

mit $1/n$ der Belichtungszeit angefunkt und auf ein und dieselbe Photoplattenstelle belichtet werden. Hierbei handelt es sich um einen vereinfachten Fall von Verfahren, die den durch Probeninhomogenität hervorgerufenen Fehleranteil durch Integration über möglichst große Teile der Probenoberfläche (z.B. durch Rotation der Probe)[8] eliminieren.

Während allen bisher angeführten Verfahren gemeinsam ist, daß die Eliminierung des Probeninhomogenitätsfehlers nur unvollkommen gelingt und deshalb in der Regel der angenäherte Analysenfehler gegenüber dem wahren Analysenfehler zu groß gefunden wird, muß erwartet werden, daß die Verfahren (4) und (5) dagegen einen zu kleinen Analysenfehler ermitteln, da sie nur die wesentlichsten Fehleranteile erfassen. Diese betreffen Plasmaschwankungen sowie Fehler der photographischen Registrierung und der photometrischen Auswertung. Andere Fehleranteile, z.B. aus Matrixeffekten und Verdampfungsunregelmäßigkeiten, werden nicht erfaßt.

Grundgedanke beider Verfahren ist es, eine Varianzanalyse aus der Messung und dem Vergleich unterschiedlicher Linienpaare eines Spektrums zu ermöglichen. In beiden Fällen wird der Gesamtfehler s (der sich aus dem Analysenfehler s_A und dem Probeninhomogenitätsfehler s_P zusammensetzt: $s^2 = s_A^2 + s_P^2$) aus dem Intensitätsverhältnis einer Linie des Analysenelementes und einer Linie des Grundelementes bestimmt (I_A/I_{B1}). Der Analysenfehler s_A wird dagegen aus dem Intensitätsverhältnis zweier Grundelementlinien ermittelt, wobei sich in diesem Schritt die Verfahren (4) und (5) unterscheiden. Während Skogerboe[8] insgesamt nur drei Linien verwendet, den Analysenfehler aus I_{B1}/I_{B2} bestimmt und damit eine Grundelementlinie in beiden Intensitätsquotienten benutzt, für die neben anderen Bedingungen insbesondere ähnliche Anregungsenergien für alle drei Linien gefordert werden, wählen Hemschik und Schuffenhauer[7] für die Bestimmung des Analysenfehlers zwei gesonderte Grundelementlinien aus (I_{B3}/I_{B4}), die sich möglichst in ihrer Anregungscharakteristik unterscheiden sollen.

Weitere Forderungen betreffen das Verhältnis der Linienintensitäten, das besonders beim Skogerboe-Verfahren möglichst nahe bei 1 liegen soll, sowie geringe Wellenlängenunterschiede der verwendeten Linien. Der Einfluß der Abweichungen von diesen Bedingungen wurde anhand unterschiedlicher Linienpaare untersucht. Aus den Ergebnissen, die in Tabelle 2 zusammengestellt sind, geht hervor, daß sich die relativen Standardabweichungen nur unwesentlich und keinesfalls signifikant voneinander unterscheiden. Auffällig ist allerdings die ungewöhnlich niedrige Streuung im Falle der Co/Cu-Intensitätsverhältnisse, die um eine ganze Grössenordnung geringer ist als die der Ni/Cu-Intensitätsquotienten.

In Tabelle 3 sind die Ergebnisse der Homogenitätsprüfung aller eingangs angeführten Analysenverfahren zusammengestellt. Für die Verfahren (1), (2), (3) und (6) wurden jeweils die Varianzen der Schwärzungsdifferenzen ΔY dem F-Test zugrunde gelegt. Beim F-Test für Homogenitätsprüfungen ist zu beachten, daß der Quotient der Varianzen stets so zu bilden ist, daß $s^2 = s_A^2 + s_P^2$ in den Zähler und s_A^2 in den Nenner gesetzt wird. Das gilt auch (in Abwei-

Tabelle 1. Anregungs- und Aufnahmebedingungen

Spektrograph	Quarzprismenspektrograph Q 24 (VEB Carl Zeiss Jena)
Spaltbreite	20 μm
Lichtführung zum Spektrographen	Zwischenabbildungssystem Zeiss, Elektroden ausgeblendet
Anregung	Funkenerzeuger FF 20 (Carl Zeiss Jena) 12000 V; 1,00 A; 6000 pF; 35 Ohm
Elektrodenanordnung	point-to-plane Technik: scheibenförmige Kupferprobe als Flächenelektroden Gegenelektrode: Reinst-Silberstab 5 mm Durchmesser, 90° Kegelstumpf angespitzt. Deckflächen-Durchmesser 1,2 mm
Elektrodenabstand	2 mm
Brennfleckdurchmesser	3 bis 4 mm
Belichtungszeit	50 sek
Photomaterial	ORWO WU 3, spektral blau extrahart.
Entwicklung	Metol-Hydrochinon 1:4 4 min Schaukelentwicklung bei 18°
Schwärzungsmessung	Schnellphotometer G II (VEB Carl Zeiss Jena)

Tabelle 2. Relative Standardabweichung in bezug auf die angegebenen Intensitätsverhältnisse für verschiedene Linienpaare mit unterschiedlicher Übereinstimmung der von Skogerboe angegebenen Bedingungen

Analytische Linienpaare	$\Delta\lambda$, nm	ΔU_i, eV	ΔY	$(I_B)/I_A$	s_{rel}
Ni II 227,0 / Cu II 229,4	2,4	1,10	0,71	5,1	0,220
Ni II 227,0 / Cu I 249,2	22,2	1,64	0,04	1,11	0,214
Ni II 227,0 / Cu II 248,6	21,6	4,32	0,28	1,91	0,203
Ni II 239,5 / Cu II 240,0	0,5	1,15	0,12	1,32	0,189
Co II 245,0 / Cu II 246,9	1,9	0,62	0,44	2,78	0,025
Co II 246,4 / Cu II 248,6	2,2	4,69	0,82	6,67	0,017
Co II 252,0 / Cu I 249,2	2,8	1,27	0,04	0,91	0,020

chung vom Normalfall des F-Tests) für die Fälle, in denen s^2 zufällig kleiner als s_A^2 erhalten wird. Die Prüfung erfolgte auf dem Signifikanzniveau $P = 0{,}95$ ($\bar{\alpha} = 0{,}05$). Bei Ablehnung der Nullhypothese wurde die dem jeweiligen F-Test entsprechende Wahrscheinlichkeit $P_F = 1 - \alpha_F$ durch Interpolation ermittelt und in Tabelle 3 zusätzlich zur Entscheidung "inhomogen" (I) angegeben.

Bei Nichtablehnung der Nullhypothese wurde das Irrtumsrisiko β für den Fehler 2. Art ermittelt[1] und in Tabelle 3 als statistische Sicherheit $P_\phi = 1 - \beta$ für die Richtigkeit der Entscheidung "homogen" (H) angegeben.

Aus Tabelle 3 geht hervor, daß für Nickel mit allen Verfahren die Entscheidung "inhomogen" erhalten wird. Dagegen sind die Aussagen für Cobalt recht unterschiedlich, wobei bemerkenswert ist, daß die erwartungsgemäß "schärferen" Testverfahren (4) und (5) die Nullhypothese nicht ablehnen. Allerdings ergibt sich aus dem Irrtumsrisiko β für den Fehler 2. Art eine sehr geringe Wahrscheinlichkeit für Homogenität.

In der Hoffnung, die teilweise widersprüchlichen Aussagen der unterschiedlichen spektrographischen Verfahren erklären zu können und eine Vorstellung von der Verteilung des Nickel und des Cobalts in der Kupferprobe zu erhalten, wurden elektronenstrahlmikroanalytische Untersuchungen der Probe vorgenommen. In Abb. 2 sind zunächst die Konzentrationsprofile von Cobalt und Nickel dargestellt, die durch Linienanalyse über eine Strecke von 1 mm erhalten wurden. Zweierlei fällt auf:

1. Konzentrationsänderungen von Nickel und Cobalt verlaufen synchron und völlig gleichsinnig;
2. die absoluten Schwankungsbreiten von Nickel und Cobalt sind etwa gleich, sie liegen ungefähr bei 0,5 M – %. Aufgrund des geringeren Nickelgehaltes sind dessen relative Gehaltsschwankungen jedoch größer (37% gegenüber 19% bei Cobalt).

Durch Ermittlung der Abhängigkeit zwischen s^2 und dem Brennfleckdurchmesser D wurde die kritische Brennfleckgröße $D_{Krit} = 110$ µm bestimmt,[3] oberhalb derer keine Inhomogenitäten mehr nachweisbar sein sollten.

Abbildung 3 zeigt, daß bei einer Linienanalyse mit $D = 120$ µm tatsächlich zunächst, und zwar innerhalb des Probengebietes, in dem D_{Krit} bestimmt wurde, die Konzentrationsschwankungen innerhalb der angegebenen Konfidenzintervalle liegen. Das ändert sich nach Durchlaufen einer Strecke von etwa 500 µm plötzlich, die Konfidenzintervalle werden nun beträchtlich überschritten. Offensichtlich stellt die untersuchte Probe ein recht kompliziertes Mehrstoffsystem dar, bei dem Schwankungen in Mikrobereichen von Schwankungen in größeren Probenbezirken überlagert sind. Man muß zur Erklärung dieser Phänomene wahrscheinlich unterschiedliche Stufen oder Grade von Homogenität in der untersuchten Probe annehmen. Diese Befunde sind möglicherweise auch für die nicht in jedem Fall übereinstimmenden Aussagen der unterschiedlichen spektrographischen Verfahren maßgebend.

Für eine umfassende Beteilung der in dieser Arbeit

Tabelle 3. Ergebnisse der Homogenitätsprüfung einer cobalt-nickeldotierten Kupferprobe nach verschiedenen Analysenverfahren. Ergebnisangabe: *F-Wert*: *I* bzw. *H* ($1 - \alpha$ bzw. $1 - \beta$)

Analysenverfahren	Nickel	Cobalt	F_{Krit} (0,95)
(1) Anfunkung von vier nicht benachbarten Anfunkungen	29:*I*(0,990)	6,6:*H*(0,5)	9,28
(2) Vierfache Anfunkung an ein und derselben Probenstelle	306:*I*(0,997)	27:*I*(0,988)	9,28
(3) Örtliche Integration Vielfleckmethode ($n = 4$)	35:*I*(0,992)	25:*I*(0,987)	9,28
(4) Hemschik und Schuffenhauer (*a*) I_A/I_B	28:*I*(0,999)	2,07:*H*(0,72)	3,44
(*b*) ΔY	17:*I*(0,999)	1,18:*H*(0,65)	
(5) Skogerboe (*a*) I_A/I_B	28:*I*(0,999)	2,04:*H*(0,70)	3,44
(*b*) ΔY	16:*I*(0,999)	1,05:*H*(0,62)	
(6) Anfunkung an undotierter Probenstelle	49:*I*(0,996)	4,2:*H*(0,5)	9,28

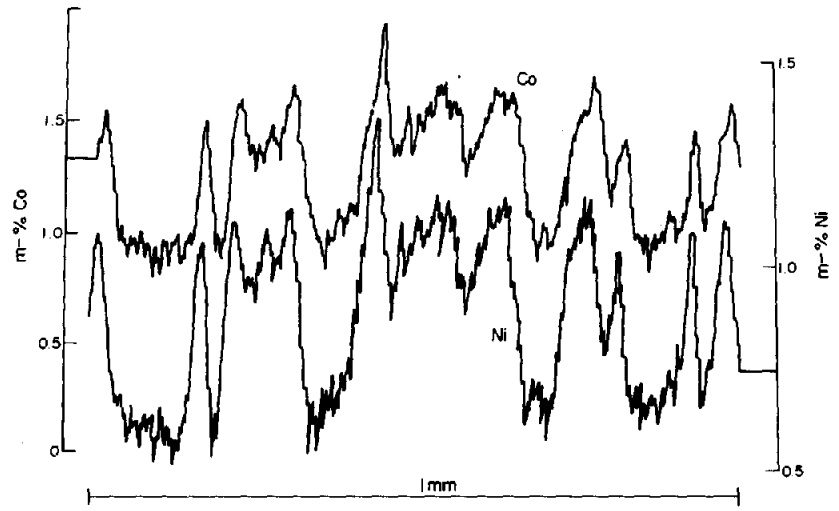

Abb. 2. Konzentrationsprofil einer Linienanalyse über 1 mm mit der Elektronenstrahlmikrosonde JEOL JXA-3A (U_A = 25 kV, v = 50 μm/min, Strahldurchmesser D = 20 μm).

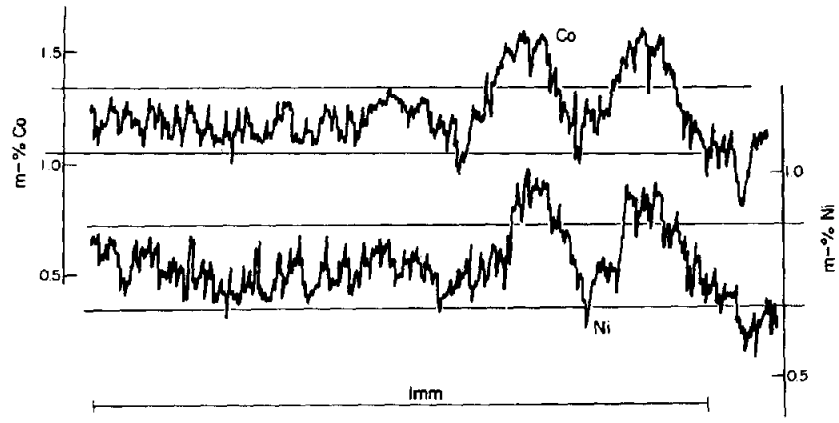

Abb. 3. Konzentrationsprofil einer Linienanalyse über 1 mm mit eingezeichneten Konfidenzgrenzen (JXA-3A, U_A = 25 kV, v = 50 μm/min, D = 120 μm).

verglichenen Verfahren sind weitere Untersuchungen erforderlich, zweckmäßigerweise an Mehrstoffsystemen, deren struktureller Aufbau nicht so kompliziert ist wie im hier vorliegenden Fall.

Für die Bereitstellung der untersuchten Kupferprobe und der verwendeten Reinstsilber-Gegenelektrode möchten wir an dieser Stelle den Herren Dr. Tölle, Dr. Ehrhardt und Dr. Geißler vom Forschungsinstitut für NE-Metalle Freiberg (DDR) danken. Herrn Doz. Dr. Heckendorff vom Wissenschaftsbereich Wahrscheinlichkeitstheorie und Statistik der Sektion Mathematik der Technischen Hochschule Karl-Marx-Stadt sind wir für klärende Diskussionen zu statistischen Grundlagen der hier behandelten Probleme zu Dank verpflichtet.

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Summary—A number of methods using optical emission spectrography have been compared in order to obtain some measure of the analytical error of this technique. They include (1) measurement at several spots at closely adjacent positions on one sample; (2) measurement by repeated sparking at one position on the sample; (3) local averaging of measuued values obtained by the multiple-spot method; (4) the line-pair method of Hemschik and Schuffenhauer; (5) Skogerboe's three-line method. The results are compared amongst themselves and also with some electron microprobe measurements on the same sample.

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THE DIFFERENTIAL PULSE POLAROGRAPHIC DETERMINATION OF TRACE AMOUNTS OF TIN AND ITS APPLICATION TO ZINC–ALUMINIUM ALLOYS

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Summary—A differential pulse polarographic procedure for the determination of 0.001–0.02% of tin in zinc–aluminium alloys is described. The tin is first separated from interfering elements such as copper and lead by homogeneous co-precipitation with aluminium succinate. The tin is determined polarographically in a 1*M* hydrochloric acid + 4*M* ammonium chloride electrolyte. After the tin has been masked with alkaline citrate a second polarogram is recorded to ascertain whether residual lead is present and, if so, a correction is applied.

As part of a research programme investigating the properties of certain zinc–aluminium alloys it was necessary to determine small amounts of tin, *i.e.*, less than 0.02%, in the alloys.

Polarographic methods for the determination of tin are well known[1–3] and have been applied to ores, steels and alloys as well as to other materials. Most of the methods reported[4–9] employed normal d.c. polarography for determination of the tin after its preliminary separation from various interfering elements, but they were not sufficiently sensitive for the samples in which we were interested unless a large sample were taken, and this was not practical, partly because of the high aluminium content and partly for other reasons.

The advent of more sensitive polarographic techniques, such as differential pulse polarography, has extended the technique to allow smaller amounts of a desired element to be determined, or smaller amounts of sample to be taken for the determination. Bhowal and Umland[10] determined small amounts of tin by differential pulse polarography after extraction of the tin as its *N*-benzoylphenylhydroxylamine complex into chloroform. The chloroform extract was subjected to polarography directly after the addition of water and a methanolic solution of lithium perchlorate. A study of the effect of diverse elements showed that up to 200–250 times as much aluminium, copper or zinc as tin could be tolerated in the extraction step. Molybdenum(V), vanadium(V) and titanium(V) were co-extracted and interfered. No application of the method to the analysis of any kind of sample was reported. This procedure, while attractive in principle, did not appear to be applicable to zinc–aluminium–copper alloys because of the much higher ratio of these elements to tin in the alloys.

As a brief search of the literature failed to reveal any reference to the differential pulse polarographic determination of tin in zinc–aluminium alloys, an investigation was undertaken to develop a suitable procedure: this report describes its successful application to the determination of 0.001–0.2% tin in zinc alloys containing about 12% of aluminium and small amounts of copper and lead.

EXPERIMENTAL

Apparatus

PAR Model 174 Polarographic Analyzer with Model 174/70 drop-timer, and Houston Omnigraphic Model 2000 X-Y recorder equipped with Type 3, X and Y modules, Princeton Applied Research Corp., N.J., U.S.A.

Dropping mercury electrode assembly.

Water-bath equipped with thermostat to maintain a temperature of 25.0 ± 0.1°.

Millipore filtration unit, 250-ml size, with Millipore filter discs, HAWP 04700, 47 mm diameter, 0.45 μm porosity, Millipore Filter Corp., Bedford, Mass., U.S.A.

Micropipettes, various sizes, 10–300 μl. Centaur Chemical Co., Stamford, Conn., U.S.A.

Analytical procedure

Dissolution of sample and homogeneous precipitation of tin. Transfer an accurately weighed 2-g sample of the alloy to a covered 400-ml beaker and dissolve it in 20–25 ml of 6*M* hydrochloric acid. Warm the solution gently to aid dissolution of the last traces of the soluble metals. Then add a few drops of 30% hydrogen peroxide to dissolve the copper and finally boil gently for a short time to remove the excess of peroxide and to ensure the dissolution of any precipitated tin. Keep the beaker covered at all times to avoid loss of tin. Dilute the solution to about 150 ml with water and add 4 g of hydroxylamine hydrochloride and 10 g of ammonium chloride. Boil the solution

gently for a few minutes to reduce the copper(II) to copper(I). Add 5 g of succinic acid and 4 g of urea, stir to dissolve, and dilute to 250 ml with water. Add concentrated ammonia solution dropwise to bring the pH to about 3.5. Boil the solution gently for 2 hr to precipitate the aluminium. A boiling stick placed in the solution helps to prevent bumping at this stage. Filter the solution hot through a Millipore filter and quickly wash the beaker and the precipitate on the filter four or five times with a hot wash solution containing 1% of succinic acid and 1% of hydroxylamine hydrochloride and neutralized to Methyl Red by addition of ammonia. It is not necessary to remove all the precipitate adhering to the wall of the beaker. Disconnect the Millipore unit and transfer the precipitate to the original beaker with a few ml of water. Add 20 ml of water containing 7.0 ml of concentrated hydrochloric acid (Note 1) to the precipitate and warm gently on the hot-plate until the precipitate is completely dissolved, swirling the beaker occasionally to dissolve the precipitate on the wall of the beaker. Cool the solution slightly and transfer it to a 50-ml standard flask containing 10 g of solid ammonium chloride, rinsing the beaker with a small amount of water. Mix the solution in the flask to dissolve the ammonium chloride, make up to the mark at 25.0° and mix thoroughly.

Polarographic determination of tin and preparation of the tin and lead calibration curves. Pipette a 10.0-ml aliquot of the solution into a dry polarographic cell and deaerate with nitrogen. Immerse the dropping mercury electrode in the solution and record the differential pulse polarogram from −0.2 to −0.8 V *vs.* SCE at a suitable current and sensitivity and at a scan-rate of 2 mV/sec, a modulation amplitude of 50 mV and a drop-time of 1 or 2 sec. After recording the tin-plus-lead peak at −0.51 V *vs.* SCE, add 1.0 ml of 50% ammonium citrate solution, 2.0 ml of concentrated ammonia solution and pass nitrogen through the solution to mix and deaerate it. Record a second polarogram at the same instrumental settings to obtain the lead peak at −0.54 V *vs.* SCE.

The height of the lead peak obtained in the second polarogram is not the same as it would be on the first polarogram, because of the dilution. Moreover, an equal concentration of lead in the two solutions does not give identical peak heights because of differences in the diffusion current constants. Thus it is necessary to compute an equivalent current due to lead in the acidic chloride solution from its measured current in the ammoniacal citrate solution. In addition, the aluminium succinate exerts a slight depressive effect on the tin and lead peaks in the two electrolytes and it should be included in the solutions used for the preparation of the calibration curves.

These curves are obtained as follows. Prepare a solution containing 0.25 g of pure aluminium (Note 1) and carry it through the basic succinate precipitation step of the procedure. Filter off and dissolve the basic aluminium succinate and make it up to 50 ml in 1*M* hydrochloric acid and 4*M* ammonium chloride solution in the same manner as for the samples. Transfer a 10.0-ml aliquot of the solution to a polarographic cell, deaerate it with nitrogen and record a "blank" polarogram. Add small increments, *e.g.*, 0.01–0.20 ml, of a standard tin(IV) solution (0.2 mg Sn/ml) by means of micropipettes and record a polarogram after each addition. Plot the current peak height *vs.* the tin concentration. Using a second 10.0-ml aliquot of the solution, plot a similar calibration curve for small amounts of lead. Take a third 10.0-ml aliquot portion, add 1.0 ml of 50% ammonium citrate solution and 2.0 ml of concentrated ammonia solution and add small increments of a standard lead solution as before, to obtain the calibration curve for lead in the ammoniacal citrate medium. From the three calibration curves obtain the necessary conversion factors for the calculations (Note 2).

Calculations. By means of the factor derived from the calibration curves convert the current due to lead in the ammoniacal citrate medium (second polarogram) into the equivalent current in the acidic chloride medium. Deduct this computed current from the combined currents of tin and lead in the acidic chloride medium (first polarogram) to obtain the net peak current for tin. From this net peak current calculate the tin content of the samples by using factors derived from the tin calibration curve.

Notes

1. The amount of acid used is just sufficient to dissolve the amount of aluminium precipitated (0.25 g) and to provide the necessary excess of hydrochloric acid in the final solution. If a different amount of aluminium is present the amount of hydrochloric acid taken must be adjusted accordingly.

The amount of aluminium used in the preparation of the calibration curves corresponds to the amount in the 2-g samples of zinc–aluminium alloy under investigation in this report. For other alloys the amount of aluminium in the standards for the calibration curves should be matched to that in the alloys. For samples low in aluminium, an appropriate amount may be added. Alternatively, a larger sample weight may be used, in which case it should be possible to determine even lower percentages of tin.

2. If only a few samples are to be analysed, the tin concentration in the supporting electrolyte may be determined by the method of standard additions. This technique is relatively simple and avoids the need to prepare a calibration curve, but is satisfactory only in the absence of lead.

PRELIMINARY TESTS

Initial attempts to determine the tin by differential pulse polarography directly in solutions of the zinc–aluminium alloy in 1*M* hydrochloric acid plus 4*M* ammonium chloride were unsatisfactory for several reasons. In the dissolution process the bulk of the copper was left as the metal but a certain amount was dissolved and interfered with the measurement of the tin and lead peaks on the polarograms.

The use of masking agents such as thiourea, EDTA, cyanide, *etc.*, to mask the copper was not successful, either because of the large amounts of zinc and aluminium present, or because the tin was also masked. Removal of the copper by controlled-potential electrolysis at either a platinum or a mercury cathode also proved unsuccessful because small but interfering amounts remained in solution even after prolonged electrolysis. Moreover, this technique had the disadvantage that it was too time-consuming.

Co-precipitating the tin along with the aluminium by adding an excess of ammonia solution was unsatisfactory because the precipitate was extremely voluminous, gelatinous and very difficult to filter off and wash. Moreover, a considerable amount of copper was also adsorbed on the precipitate and was impossible to remove completely either by washing or by reprecipitation. By use of homogeneous precipitation of the aluminium as the basic succinate, as advocated by Willard and Tang,[11,12] these difficulties were overcome and dense, easily collected precipitates were obtained.

Table 1. Determination of tin in synthetic zinc–aluminium solutions* by differential pulse polarography after co-precipitation with basic aluminium succinate

No. of detns.	Lead added, *mg*	Tin added, *μg*	Tin found,† *μg*
1	Nil	20	16
2	Nil	40	40 ± 1
2	0.5	40	40 ± 3
2	5.0	40	37 ± 1
2	Nil	80	80 ± 0
1	Nil	120	115
1	Nil	160	157
2	Nil	200	197 ± 2
1	Nil	300	300
8	Nil	400	403 ± 16
2	0.5	400	398 ± 11
2	5.0	400	402 ± 14

* Each synthetic sample contained 2 g of zinc, 0.25 g of aluminium and 0.025 g of copper.
† Standard deviation 8 μg.

RESULTS AND DISCUSSION

The procedure described above was applied to synthetic solutions containing 2 g of zinc, 0.25 g of aluminium, 25 mg of copper and 20–400 μg of tin, and it was established that the tin was quantitatively precipitated with the aluminium succinate. In some experiments amounts of lead ranging from 0.5 to 5 mg were added to see whether it was also co-precipitated. The tin was finally determined in 1*M* hydrochloric acid plus 4*M* ammonium chloride solution by differential pulse polarography. The results of these experiments are given in Table 1.

The standard deviation *s* at the 400 μg level was 8 μg. Only one precipitation was necessary and examination of the polarograms revealed that the separation from copper and lead was excellent. The amount of copper co-precipitated with the aluminium and tin was in nearly all cases less than 0.5 μg per ml of supporting electrolyte, *i.e.*, the 25 mg of copper originally present had been reduced to less than 25 μg. This amount of copper had virtually no effect on the height of the tin peak. Moreover, other experiments indicated that a copper concentration up to at least 1.5 μg/ml in the supporting electrolyte could be tolerated in the determination of tin at the 0.5 μg/ml level; in other words the tolerance was at least 3 times as much as the copper level found in the final solution after the precipitation step.

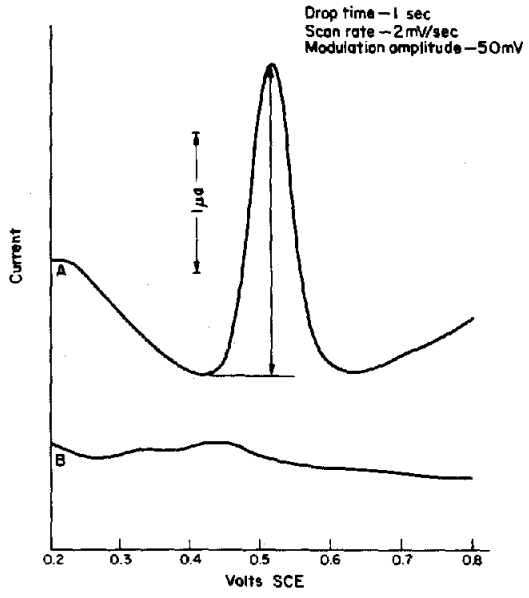

Fig. 1. Differential pulse polarogram of tin after co-precipitation with basic aluminium succinate. A: Sn 40 μg in 10 ml of 1*M* hydrochloric acid + 4*M* ammonium chloride; B: after addition of 1 ml of 50% ammonium citrate and 2 ml of ammonia solution.

The amount of lead in the precipitate was usually less than the limit of detection, *i.e.*, about 0.1 μg per ml of supporting electrolyte at an instrumental sensitivity of 1 μA for full-scale deflection. Because negligible amounts of lead were co-precipitated with the aluminium and tin it was therefore not usually necessary to correct the height of the tin peak obtained in the acidic ammonium chloride electrolyte for the presence of lead. Nevertheless, a polarogram was recorded each time after the addition of alkaline citrate solution simply to confirm the absence of lead.

A typical polarogram is shown in Fig. 1. The peak at −0.44 V on the polarogram B is due to the presence of a trace of copper. In polarogram A this copper peak would also occur and contribute to the current at −0.3 V but would not affect the tin peak at −0.52 V and therefore does not interfere.

During the investigation it was necessary to overcome some difficulties in technique. For example, when an ordinary filter paper was used to collect the basic aluminium succinate it was found that some of the precipitate remained embedded in the pores of the filter and could only be removed by thorough washing with hot hydrochloric acid. This made it difficult to keep the volume of the final solution sufficiently low before transfer to the 50-ml standard flask and often the solution had to be evaporated. On the other hand, ignition or destruction of the paper with nitric and perchloric or sulphuric acids was not practical. The use of a Millipore filter, however, was very convenient and had several advantages over the use of ordinary filter paper. The granular nature of the precipitate enabled it to be filtered off quickly and because of the small size of the filter disc, fewer washings were required to remove completely the extraneous impurities, especially copper. The precipitate was easily removed from the disc and transferred to the original beaker with only a small amount of water. The greater initial cost of the Millipore filter discs was offset by the fact they that could be used several dozen times, if necessary, before being discarded.

In other preliminary experiments it was found that recoveries of tin were low by about 10–15% owing to depression of the peak by the aluminium succinate

Table 2. Composition of zinc–aluminium alloys

Element	Nominal%
Al	12
Mg	0.02
Cu	1.0–1.5
Si	<0.01
Pb	0.001–0.02
Sn	0.001–0.02
Zn	Balance

present. These apparently low recoveries were overcome by preparing a calibration curve with solutions containing the same amount of aluminium succinate as the sample solutions. In this work the amount of aluminium present was dictated by the size of sample required (2 g) to give a measurable amount of tin. All the alloys contained approximately the same percentage of aluminium and since a similar weight of sample was taken for each analysis the final aluminium concentration was relatively constant.

The height of the tin peak thus depends to some extent on the concentrations of aluminium succinate in the supporting electrolyte. Therefore, if other applications of the method are contemplated, in which the aluminium may be absent or present in greatly variable amounts, it will be necessary, prior to the precipitation step, to adjust the amount of aluminium present to provide an arbitrary but approximately constant amount for each sample, *e.g.*, by taking suitable sample weights or adding appropriate amounts of pure aluminium. The calibration curve should likewise be prepared from solutions having similar concentrations of aluminium. Alternatively, the standard-addition technique may be used to determine the tin concentration.

Table 3. Determination of tin in zinc–aluminium alloys by differential pulse polarography after co-precipitation with basic aluminium succinate

Sample	Tin found, %
A	0.0018, 0.0018
B	0.0028, 0.0030
C	0.0017, 0.0016
D	0.0160, 0.0160
E	0.0011, 0.0012
F	0.0012, 0.0012
G	0.0030, 0.0031
H	0.0031, 0.0021
I	0.0009, 0.0007
J	0.0019, 0.0027
K	0.0008, 0.0009

The procedure finally adopted was applied to the zinc–aluminium alloys submitted for analysis. The nominal composition of these alloys is given in Table 2. Duplicate individually weighed 2-g samples were taken for analysis and the results are given in Table 3.

Conclusion

The results of the investigation show that the proposed method is suitable for the determination of tin in zinc–aluminium–copper alloys, at the level indicated, with good precision. No results obtained by alternative methods were available for comparative purposes but the results on synthetic samples indicate that the values obtained can be considered reliable. The combination of precipitation from homogeneous solution with differential pulse polarography results in a method which is highly selective, sensitive and free from interference by other constituents of the alloys. The method should also be applicable to other alloys, steels, and tin ores and need not be restricted to small amounts of tin.

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NEW CHROMOGENS OF THE FERROIN TYPE—IX 2-PYRIDYL AND PYRAZINYLHYDRAZONES OF SOME PYRIDYL, PYRAZINYL AND PYRIDAZINYL KETONES AND OF ISATIN AND PHENYLGLYOXAL

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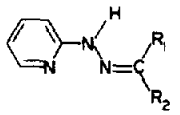
Summary—Chromogenic properties of 22 new hydrazones, all ferroin-type compounds, have been evaluated with respect to iron(II), copper(I), cobalt(II) and nickel(II). Some show promise as sensitive reagents for the determination of trace amounts of these metal ions. Stoichiometric ratios were determined for the iron(II) chelates and interpreted to distinguish between *syn*- and *anti*-isomers.

Several years ago a number of 2-pyridyl and pyrazinylhydrazones were prepared by Case[1] for the purpose of providing new reagents with chelating properties for iron(II) and copper(I). A detailed study of the chromogenic reaction of these ferroin-type reagents with iron(II), copper(I), cobalt(II), and nickel(II) has now been completed, and the results are presented in this communication.

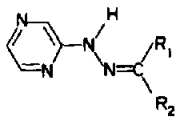
The compounds are identified below by type, structure, and/or name with Roman numeral designations for ease of reference.

2-Pyridylhydrazones



	R_1	R_2
I	Methyl	Pyrazinyl
II	Phenyl	Pyrazinyl
III	Methyl	3-Pyridazinyl
IV	2-Pyridyl	2-Pyridyl

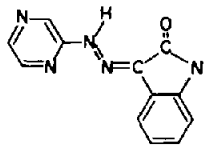
Pyrazinylhydrazones



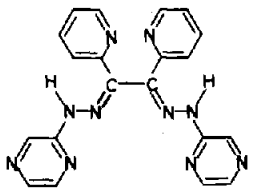
V	Hydrogen	2-Pyridyl
VI	Methyl	2-Pyridyl
VII	Phenyl	2-Pyridyl
VIII	2-Pyridyl	2-Pyridyl
IX	Methyl	Pyrazinyl
X	Pyrazinyl	Phenyl
XI	Hydrogen	Benzoyl
XII	Phenyl	Benzoyl
XIII	2-Pyridyl	2-C_5H_4N–CO–
(Pyridil monopyrazinylhydrazone)		
XIV	Methyl	3-Pyridazinyl
XV	Phenyl	2-C_5H_4N–NH–
(*N*-2-Pyridylbenzamide pyrazinylhydrazone)		
XVI	2-C_5H_4N–NH–	2-Pyridyl
(*N*-2-Pyridylpicolinamide pyrazinylhydrazone)		

Miscellaneous hydrazones

XVII Isatin-3 pyrazinylhydrazone



XVIII 2,2′-Pyridil dipyrazinylhydrazone



XIX Isatin-3 2-pyridylhydrazone
XX Phenylglyoxal dipyrazinylhydrazone
XXI Benzoylpyrazine phenylhydrazone
XXII Phenylglyoxal di(2-pyridyl)hydrazone

EXPERIMENTAL

Spectral measurements were made with a Cary Model 14 recording spectrophotometer and corrected for absorbance due to reagent blanks. Ligand to metal ratios of the iron(II) chelates were determined spectrophotometrically by the mole-ratio method.[2,3] Standard solutions, buffers, reagents, and procedures used in this investigation were those described previously.[4]

Solutions of the metal chelates prepared for spectral measurements were buffered at pH 7 (if not otherwise specified) with ammonium acetate and contained 50% ethanol (v/v) to ensure complete dissolution of ligand and complex.

RESULTS AND DISCUSSION

With few exceptions the new compounds formed coloured iron(II) chelates over the pH range 3–11. Colour changes occurred on changing the pH from 4 to 7, with absorption bands shifting to longer wavelengths. Such changes could arise from ionization of

Table 1. Absorption properties of copper(I), cobalt(II) and nickel(II) chelates

Ligand	Copper(I)			Cobalt(II)			Nickel(II)		
	Colour	λ, nm	ϵ, $l.mole^{-2}.cm^{-1}$	Colour	λ, nm	ϵ, $l.mole^{-1}.cm^{-1}$	Colour	λ, nm	ϵ, $l.mole^{-1}.cm^{-1}$
I	Orange	500	5.2×10^3	Magenta	525	2.18×10^4	Orange	497	2.26×10^4
II	Orange	519	1.09×10^4	Magenta	538	2.48×10^4	Red-orange	512	3.40×10^4
III	Orange	481	5.0×10^3	Orange-red	519	1.90×10^4	Yellow	475	1.15×10^4
IV	Yellow-orange	479	1.01×10^4	Orange	492	3.30×10^4	Yellow	466	3.20×10^4
V	Yellow-orange	481	1.77×10^4	Orange	495	2.70×10^4	Yellow	488	4.30×10^4
VI	Yellow	475	1.66×10^4	Orange	480	2.40×10^4	Yellow	460	3.75×10^4
VII	Orange	494	2.02×10^4	Red-orange	502	2.76×10^4	Yellow	475	4.10×10^4
VIII	Orange	495	2.07×10^4	Red-orange	505	3.07×10^4	Yellow	481	4.58×10^4
IX	Red-orange	511	1.54×10^4	Magenta	528	2.20×10^4	Orange	498	3.55×10^4
X	Orange-yellow	519	$3.0 \times 10^{3*}$	†	†	†	†	†	†
XI	Orange	470	$2.0 \times 10^{3*}$	Orange	485	$8.4 \times 10^{3*}$	Yellow	487	$6.50 \times 10^{4*}$
XII	Yellow-orange	467	230*	Yellow-orange	475	$8.3 \times 10^{3*}$	Orange	504	$5.50 \times 10^{4*}$
XIII	Orange	504	1.90×10^4	Orange	507	2.72×10^4	Orange	483	4.30×10^4
XIV	Orange	500	1.50×10^4	Magenta	525	2.08×10^4	Yellow	480	3.00×10^4
XV	Yellow	422	4.2×10^3	Yellow	446	1.10×10^4	†	†	†
XVII	†	†	†	†	†	†	†	†	†
XVIII	Orange	484	2.00×10^4	Red-orange	508	2.97×10^4	Yellow	479	4.60×10^4

* Beer's law not followed.

† Colour and spectrum very similar to that of free ligand.

the hydrogen atom from the hydrazone moiety of the co-ordinated ligands.

The most sensitive iron(II) chromogen of the group is **XII**; however, it forms a relatively weak iron(II) chelate so a moderately large excess of chromogen is necessary for quantitative results. More sensitive ferroin reagents are available for the determination of iron, and it is unlikely that **XII** or any of the hydrazone derivatives will supplant them.

Compounds **X**, **XVII** and **XIX–XXII** failed to form iron(II) chelates, presumably because of steric hindrance. For this reason these hydrazones are believed to exist predominantly as *syn*-isomers, *i.e.*, the two potentially co-ordinating groups are in a *syn*- or *cis*-configuration about the >C=N– group of the hydrazone. The presence of a bulky non-co-ordinating group in an *anti*-configuration (the R_2 group in the structures depicted above) should sterically discourage chelation of iron(II) by more than one ligand molecule, thus preventing formation of a characteristically coloured ferroin-type tris-chelate of iron(II). Thus the isomer structures assigned above for **X** and **XVII** are believed to be correct. Compound **XIX**, for the same reason, probably has the same configuration as **XVII**. Similar distinctions concerning which isomer (*syn*- or *anti*-) predominates in **XX**, **XXI** and **XXII** are less conclusive owing to the greater complexities of their structure and the several possible ways for them to act as chelating agents.

Copper(I), cobalt(II) and nickel(II) gave chromogenic reactions with most of the new compounds over the pH range 3–11, with maximum colour formation in the pH region 5–11. Unlike the iron(II) chelates, the complexes gave no colour changes on change of pH. Most of the copper(I) chelates proved readily extractable with isoamyl alcohol but the other metal chelates were only partially extracted. As expected from previous studies,[5–7] the copper, cobalt and nickel chelates each exhibited a single, broad intense absorption band in the visible spectrum. The wavelength of maximum absorbance, molar absorptivity, and colour of each chelate are listed in Table 1. Of the new compounds investigated, **IV** and **VIII** merit special attention as sensitive chromogenic reagents for nickel, cobalt, and copper. Their high molar absorptivities and differences in wavelengths of maximum absorbance should enable trace amounts of these metals to be determined in the presence of one another. Further investigation of these is contemplated.

Results of mole-ratio studies for the iron(II) chelates, compiled in Table 2 along with spectral data, are of interest as a means of identifying the stoichiometry and relative stability of the chelates and of distinguishing between certain possible structures or configurations for the ligands. For example, compounds **I–III**, **V–VII** and **XIV** all formed bis-chelates of iron(II) of relatively high stability, as evidenced by

Table 2. Absorption properties and ligand to metal mole-ratios of iron(II) chelates

Ligand	pH 4			pH 7			
	Colour	λ, nm	ϵ, $l.mole^{-1}.cm^{-1}$	Colour	λ, nm	ϵ, $l.mole^{-1}.cm^{-1}$	L/Fe
I	Magenta	550	7.3×10^3	Brown	598	3.7×10^3	1.90[s]
					430*	1.43×10^4	
II	Magenta	554	9.0×10^3	Brown	633	6.6×10^3	2.07[s]
					450*	2.30×10^4	
III	Orange	535	7.4×10^3	Red	537	6.8×10^3	2.26[s]
					458*	7.5×10^3	
IV	Magenta	537	1.31×10^4	Red	538	1.04×10^4	2.02[s]
V	Orange	520	5.3×10^3	Red	555	5.3×10^3	2.10[s]
VI	Orange	523	6.6×10^3	Red	560	5.8×10^3	2.07[s]
VII	Red	567	7.6×10^3	Brown	570	7.5×10^3	2.11[s]
VIII	Red	575	9.2×10^3	Green	597	9.4×10^3	2.02[s]
IX	Red	583	5.4×10^3	Green	618	4.1×10^3	2.06[s]
X	Colourless	—	—	Colourless	—	—	—
XI	Gold	450*	1.8×10^3	Brown	475*	1.85×10^4	2[vw]
XII	Colourless	—	—	Orange	717	9.0×10^3	2.0[w]
					475*	2.26×10^4	
					408	2.44×10^4	
XIII	Brown	598	6.4×10^3	Brown	598	7.1×10^3	1.93[m]
		464*	1.60×10^4		487*	1.30×10^4	
XIV	Orange	571	5.1×10^3	Green	608	4.5×10^3	2.17[m]
		444*	1.38×10^4		456*	1.35×10^4	
XV	Orange	438*	7.1×10^3	Orange	425*	9.1×10^3	2.24[s]
XVI	Magenta	514	7.6×10^3	Brown	576	7.3×10^3	2.10[s]
XVII	Colourless	—	—	Colourless	—	—	—
XVIII	Green	601	1.03×10^4	Green	603	9.2×10^3	3.04[m]
		450*	1.90×10^4		455*	1.60×10^4	

* Shoulder.
[s] Strong complex; linear mole-ratio plot.
[m] Moderately strong complex; slight curvature in mole-ratio plot.
[w] Weak complex; appreciable curvature in mole-ratio plot.
[vw] Very weak complex; extreme curvature in mole-ratio plot.

the sharp intersection and linearity of their mole-ratio plots. These ligands therefore must possess a configuration that permits terdentate action. Models show that only the *anti*-isomers of these compounds can act in such a manner. The *syn*-isomers should be capable of bidentate action, but only with difficulty, owing to the presence of bulky substituents adjacent to the ferroin group.

Compounds **IV** and **VIII** exist in only one form (since $R_1 = R_2$), and both act as strong terdentate ligands in chelating iron(II). They possess the same functionality or structural features as the *anti*-isomers of the compounds just discussed (**I–III**, *etc.*).

Ligands **XI–XIII** form iron(II) chelates with a ligand to iron ratio of 2:1. Since iron(II) is hexacoordinate, presumably the carbonyl oxygen atom in each ligand co-ordinates to iron to form a 5-membered chelate ring. Consistent with theoretical expectation, co-ordination of oxygen is weak and the mole-ratio plots for XI–XII show considerable curvature. The relative order of stabilities found for their iron(II) chelates is **XI** < **XII** < **XIII**, which is reasonable in light of the electron-donor tendencies of their respective R_1 substituent groups: H < phenyl < pyridyl.

Compound **XV** acts as a terdentate ligand and therefore must possess the structure indicated above. To do so it must utilize the pyridyl nitrogen atom (in the R_2 group) to form a 6-membered chelate ring with iron(II). This is unusual as most ferroin complexes involve 5-membered rings. The ligand to iron ratio found was in excess of 2:1, suggesting that some tris-chelate may be formed, involving bidentate ligand action.

The ligand to iron ratio for **XVI** cannot be used to assign *syn*- or *anti*-configuration to the ligand because both isomers are capable of terdentate behaviour.

It was surprising to find that **XVIII** acts as a bidentate ligand in chelating iron(II). Logically, one of four different terdentate modes might have been utilized to form a more stable chelate. Nevertheless, a stable tris-chelated iron complex was formed. A satisfactory explanation for this requires further study.

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A METHOD FOR REMOVAL OF CHLORIDE INTERFERENCE IN DETERMINATION OF ALUMINIUM BY ATOMIC-ABSORPTION SPECTROMETRY WITH A GRAPHITE FURNACE

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Summary—Methods for removal of the chloride interferences in determination of aluminium by atomic-absorption spectrometry with a graphite furnace have been investigated. Two mechanisms of chloride interference have been established. The first arises from co-ordination of the chloride to aluminium. This interference can be removed by preventing the co-ordination. The other is due to co-existing chloride salts remaining until the atomization step. This interference can be removed by volatilizing the chloride or by converting it and/or aluminium chloride into another substance such as the oxides before the atomization step. The tetra-ammonium salt of EDTA is very suitable as an additive to overcome chloride interference because of its ability to co-ordinate aluminium and other cations, and also its effect when heated.

Recently, flameless atomic-absorption spectrometry with a graphite furnace has been widely used for determination of metals because of its high sensitivity and rapidity. However, interference from cations, anions, acidity, organic substances *etc.* is encountered just as in other methods of instrumental analysis. In particular, chloride co-existing in the specimen and/or added during preparation of the sample can cause severe interference. Shaw and Ottaway[1] applied the graphite furnace method to the determination of aluminium in cast iron and low-alloy steel, and pointed out that chloride interfered, but nitric acid did not, so they used nitric acid to dissolve the sample. Person *et al.* used a mixture of hydrochloric and nitric acid to dissolve steel samples and added ammonium sulphate to overcome the interference of hydrochloric acid in aluminium determination;[2] they also discussed the interference of chloride on the basis of the gaseous equilibrium of aluminium and chlorine at high temperature.[3,4] Suppression of the signal by chloride has also been frequently observed in determination of other metals. Several mechanisms, such as formation of relatively volatile compounds,[5–7] a vapour phase process[8,9] and occlusion of analyte in the matrix,[10–12] have been proposed for chloride interference. It is generally agreed that chloride interference occurs as a result of the combination of two or more factors, including those proposed above.

However, fundamental methods for removal of chloride interference have not yet been investigated. Mechanisms of interference in atomic absorption have generally been investigated in terms of reactions in the solid and/or gaseous state in the furnace. The changes in the analyte from the time of preparation of the sample to the final atomization have not generally been considered, although during these steps, the analyte may suffer from many interactions. Accordingly, we have divided the process into three stages for investigation, namely, the solution state before the instrumental operations, the drying and ashing state, and the atomization state.

EXPERIMENTAL

Apparatus

A Varian Techtron carbon-rod atomizer model 63 was used in conjunction with a Varian Techtron model 1200 atomic-absorption spectrophotometer. A tube type of graphite cell was used and the absorption was measured under a nitrogen atomosphere. The signal was recorded with a Hitachi 056 recorder. A Hitachi aluminium hollow-cathode lamp was used as the light-source and a Varian Techtron deuterium hollow-cathode lamp for background correction. The sample was added with a 5-μl Excalibur Autopet fitted with a disposable tip.

Reagents

All solutions were prepared from analytical-reagent grade chemicals and demineralized water, and stored in

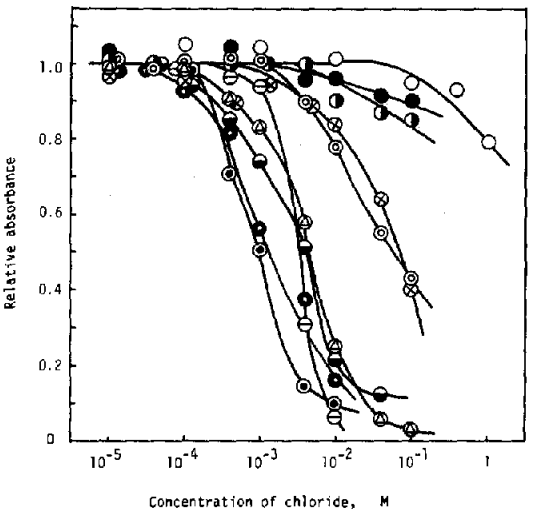

Fig. 1. Effect of chlorides on the atomic absorption of aluminium (2.5 mg/l.). ○, HCl; ●, NH_4Cl; ◎, NaCl; ⊗, KCl; ◑, $MgCl_2$; ◒, $CaCl_2$; ○, $SrCl_2$; ◉, $BaCl_2$; ⊖, $CuCl_2$; ⊘, $FeCl_3$. $FeCl_3$ at pH 1 and the others at pH 3.6.

polyethylene bottles. The 1000-mg/l. stock aluminium solution was prepared by dissolving aluminium metal (99.99% pure) and made up in 0.1*M* nitric acid.

Procedure

A 5-μl sample was deposited in the graphite tube with the micropipette and then dried, ashed and atomized with nitrogen gas flowing around the furnace at a rate of 5.5 l./min. The voltages and times for drying and atomization were kept the same: dry for 30 sec at 0.8 V (*ca.* 140°) and atomize for 4 sec at 7.0 V. The ashing step was varied. The absorption signals at 309.3 nm (0.5 nm bandwidth) were recorded and the peak-height was taken as the analytical signal. A reagent blank was run under the same conditions and a correction applied for it. The applied voltage between the atomizer terminals was measured with a digital voltmeter connected in parallel and the temperature of the graphite tube at each setting was measured with a platinum–platinum/rhodium thermocouple.

RESULTS AND DISCUSSION

Effect of chloride on atomic absorption

The interference of chloride has been widely reported. The chloride shows many kinds of behaviour, depending on the analytical conditions. The effects of chloride concentration, pH, standing time after sample preparation, furnace temperature and inert-gas flow-rate were therefore investigated.

The interference of the chlorides of H^+, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cu^{2+} and Fe^{3+} in determination of aluminium was for salt concentrations from 10^{-5} to $10^{-1}M$ in slightly acidic medium (pH 3–4) under the same ashing conditions (30 sec at 1.6 V, *ca.* 550°). As shown in Fig. 1, their interference may be classified as negligible, intermediate and extensive. The compounds in the first group are HCl, NH_4Cl and $MgCl_2$, in the second NaCl and KCl, and in the third $CaCl_2$, $SrCl_2$, $BaCl_2$, $CuCl_2$ and $FeCl_3$ (these will hereafter be referred to as the first, second and third groups).

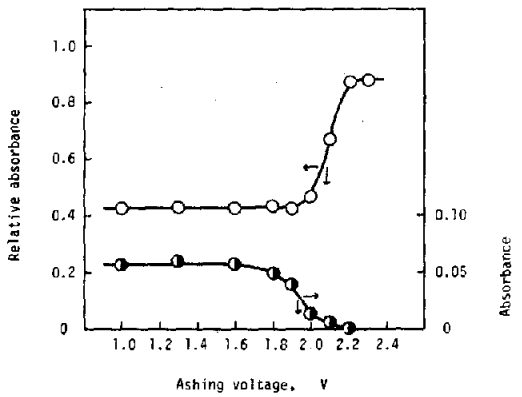

Fig. 2. Effect of ashing voltage on the atomic absorption of aluminium (2.5 mg/l) in the presence of 0.1*M* KCl. ○, Atomic absorption of Al; ◑, Molecular absorption of KCl.

The effect of varying the ashing voltage was examined and the results for solutions 0.1*M* in potassium chloride are shown in Fig. 2. With an ashing time of 30 sec the KCl molecular absorption decreases and the sensitivity for aluminium increases at above *ca.* 2.0 V (*ca.* 850°). This indicates that the interference of KCl can be removed by ashing at 2.2 V (*ca.* 1000). The interference of the sodium chloride can also be removed by controlling the ashing voltage.

The effect of the nitrogen flow-rate during the ashing step for the third group chlorides was measured, with constant nitrogen flow-rate in the atomization step. No effect of the nitrogen flow-rate was observed at low ashing voltages. However, the interference was decreased with flow-rates below 3 l./min and an ashing voltage of 2.2 V (*ca.* 1000°) for 30 sec, although it was not removed completely.

The effect of pH was examined with the pH ashing voltage set as high as possible without causing volatilization of the chloride. At pH below 5, severe suppression of the absorption were observed for all the chlorides, but the interference disappeared at pH above 9. The alkaline earth metal chlorides gave an enhancement.

The effect of standing time after addition of chloride to the sample solution is shown in Fig. 3 for 0.1*M* sodium chloride in aluminium solutions at pH 3.6

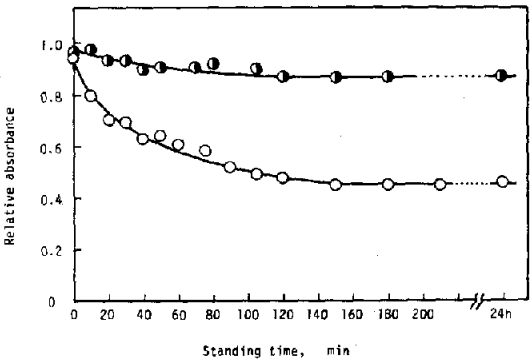

Fig. 3. Effect of standing time on the atomic absorption of aluminium (2.5 mg/l.) in the presence of 0.1*M* NaCl. ○, pH 3.6; ◑, pH 10.8.

and 10.8. For the alkaline medium, the intensity of the signals is independent of the added chloride and the standing time, but for the acidic medium, the absorbance decreases with standing time and reaches equilibrium only after about 3 hr.

The interference of the first group is almost negligible under the drying and ashing conditions used. It is considered that HCl and NH_4Cl volatilize in the drying and ashing steps, and are not present in the atomization step. Although the behaviour of $MgCl_2$ is the same, the mechanism is assumed to be different (which will be discussed later). The interference of second group salts was found to be removable by controlling the ashing temperature, but that of the third group was not. In the atomization step, the chlorides of the third group gave chloride molecular absorption. These chlorides have high vaporizing temperature, and it is assumed that they cannot be removed in the drying and ashing steps, and are still there in the atomization step.

The extent of chloride interference was found to increase with the standing time after the sample had been prepared. Aluminium frequently reacts slowly at room temperature and Fig. 3 may show that the chloride interference arises from co-ordination of chloride with aluminium. In alkaline medium, none of the chlorides cause interference, presumably because the aluminium is predominantly in the form of the tetrahydroxoaluminate anion which cannot co-ordinate chloride. Hence interference from co-ordination of the chloride can be removed by using an alkaline medium.

It is interesting that the interference of $MgCl_2$ is not as extensive as that of the other alkaline earth metal chlorides. With ashing at above *ca.* 470° the chloride interference disappeared and an enhancement occurred, similar to that of magnesium nitrate. (The enhancement effect was observed for all oxyanion salts of the alkaline earth metals, such as the nitrate, sulphate and acetate). From thermal analysis $MgCl_2.6H_2O$ is said to decompose into MgO, with an intermediate, MgClOH, formed at 459° under a nitrogen atmosphere.[14] Magnesium chloride may therefore be decomposed into magnesium oxide during ashing at temperatures higher than *ca.* 460° and may then show the same behaviour as magnesium nitrate.

Use of a low flow-rate for the nitrogen at high ashing temperature decreased the interference of the third group chlorides. The same behaviour was observed when oxygen was mixed with the nitrogen at high flow-rate. The furnace chamber used here was the open type, and oxygen from the external atmosphere may be mixed into the nitrogen around the furnace at low flow-rates of the nitrogen. Oxygen may have no effect on the chloride at low ashing temperature, but it accelerates the oxidation of the chloride salts, which probably leads to decrease in the chloride interference. Accordingly, the chloride interference may also be removable by converting the chloride into oxide by controlling the ashing temperature and nitrogen flow-rate.

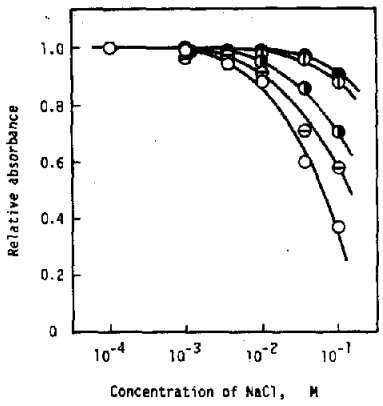

Fig. 4. Removal of NaCl interference by addition of other reagents. ○, None added; ◑, 0.1*M* HNO_3; ⊖, 0.05*M* H_2SO_4; ◑, 0.04*M* $EDTA(NH_4)_4$; ●, 0.1*M* CH_3COONH_4. Al: 2.5 mg/l.

Removal of the chloride interference

Two mechanisms of chloride interference have been pointed out in the discussion above, together with means of removing the interference. On this basis we investigated practical methods of removing the chloride interference.

The chlorides in the second group, NaCl and KCl, have a relatively low temperature of volatilization, and can be removed by controlling the ashing temperature at above 1000°. The suppression of the signal was also found to be diminished by adding chemicals, as shown in Fig. 4. The efficiency of the chemicals tried is in the order $CH_3COONH_4 > HNO_3 > EDTA(NH_4)_4 > H_2SO_4$. This trend may be explained by the combination of oxidation, co-ordination and substitution effects of the reagents. All these reagents are oxidizing in the sense that the chlorides are converted into oxides on heating, presumably because there is an anion substitution resulting in a readily volatilized chloride such as HCl and NH_4Cl, which can easily be removed in the drying and ashing steps.

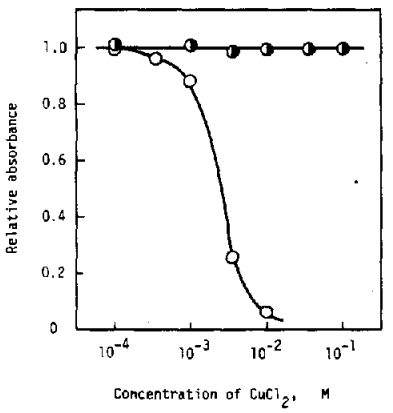

Fig. 5. Removal of $CuCl_2$ interference by addition of $EDTA(NH_4)_4$. ○, None added; ◑, 0.04*M* $EDTA(NH_4)_4$. Al: 2.5 mg/l.

Therefore, reagents such as CH_3COONH_4 and HNO_3 are suitable as addition reagents to remove the interference of intermediate type salts such as NaCl and KCl.

The third group chlorides, $CaCl_2$, $SrCl_2$, $BaCl_2$, $CuCl_2$ and $FeCl_3$, have high volatilization temperature and are difficult to remove completely in the ashing step simply by controlling the ashing conditions. With these salts, CH_3COONH_4 and HNO_3 are not as effective as for the intermediate group. This may be because these cations have a fairly high affinity for chloride which is thus less easily substituted by CH_3COONH_4 or HNO_3. As shown in Fig. 5, the interference of $CuCl_2$ is greatly removed by addition of $EDTA(NH_4)_4$. The same was observed for the other chlorides. The chelating reagents such as EDTA have high reactivity with not only aluminium but also with other cations present. In addition, the coordinated EDTA results in oxide formation on heating. $EDTA(NH_4)_4$ is very suitable for removing the interferences of the third group chlorides since the ammonium chloride produced is easily volatilized. The amount of additive needed is at least the quantity equivalent to the total metal ion content, but in practice is best determined for each case.

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ACIDITES ET COMPLEXES DES ACIDES (ALKYL-ET AMINOALKYL-) PHOSPHONIQUES—III
ALKYLPHOSPHONATES SUBSTITUES DE CALCIUM(II) ET CUIVRE(II)

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Résumé—Les constantes de stabilité des acides phosphoniques RPO_3H_2 [R = CH_3, C_2H_5, $ClCH_2$, Cl_2CH, Cl_3C, $BrCH_2$, Br_2CH, $BrCH_2CH_2$, ICH_2, $HOCH_2$, $(CH_3)_3\overset{+}{N}CH_2$] et des complexes formés RPO_3Ca, RPO_3Cu, $RPO_3Cu(OH)^-$ ont été déterminées par affinements multiparamétriques, à partir des données potentiométriques obtenues à 25°, en milieu 0,1 *M* en nitrate de potassium. La stabilité des complexes varie linéairement avec l'acidité du groupement phosphonique. Les hydroxyméthylphosphonates sont stabilisés par formation d'un cycle à cinq chaînons. La charge positive permanente de l'acide triméthylammoniumméthylphosphonique atténue, par répulsion avec le cation, la stabilité des complexes.

La connaissance des propriétés acides et complexantes du groupement phosphonique $-PO_3H_2$ présente une importance certaine dans le domaine de la biochimie et dans les applications industrielles des acides phosphoniques. En effet des acides aminoalkylphosphoniques ont été isolés à partir d'organismes vivants et de nombreuses molécules polyphosphoniques sont synthétisées, étudiées et utilisées pour leurs propriétés sequestrantes (composants des détergents et adoucissants, traitements de surface, antidotes de certains métaux, médication de la lithiase rénale...). D'autres acides phosphoniques trouvent des applications analytiques dans les extractants, les échangeurs d'ions, les réactifs.

Avant d'entreprendre les déterminations relatives aux acides aminoalkylphosphoniques, nous nous limitons, dans cet article, à des acides phosphoniques plus simples ne comportant pas de fonction amine. Paradoxalement, la description de leur pouvoir complexant n'a été qu'esquissée: on ne relève dans la bibliographie que quelques constantes de stabilité relatives aux complexes de Be(II) avec les acides (chlorométhyl- et méthyl-) phosphoniques;[1] de Am(III), Cm(III), Pm(III) avec les acides méthylphosphonique[2] et hydroxyméthylphosphonique[3] ainsi que de terres rares avec l'acide méthylphosphonique.[4] Leurs constantes d'acidité sont mieux connues, mais sont malheureusement souvent approximatives (voir tableau 1). Différents sels ou complexes de l'acide méthylphosphonique[5–11] ou de ses esters,[12–15] de l'acide hydroxyméthylphosphonique[16] sont isolés: ils conduisent généralement à des études spectroscopiques. Cependant, Manevich *et al.*[10] décrivent les dosages potentiométriques de méthylphosphonates de potassium, sodium, cadmium, strontium et plomb. Rappelons qu'un travail antérieur[17] nous a permis de suivre l'évolution de la stabilité des complexes de l'acide chlorométhylphosphonique suivant la nature du cation.

Nous nous intéresserons ici aux acidités d'un large éventail d'acides alkylphosphoniques substitués RPO_3H_2 [R = CH_3, C_2H_5, $ClCH_2$, Cl_2CH, Cl_3C, $BrCH_2$, Br_2CH, $BrCH_2CH_2$, ICH_2, $HOCH_2$, $(CH_3)_3\overset{+}{N}CH_2$] et aux espèces formées avec les cations Ca^{2+} et Cu^{2+}. Les valeurs des constantes d'acidité et de stabilité, outre leur intérêt descriptif, doivent nous permettre par la suite de dégager les paramètres qui influent sur le pouvoir complexant du groupement phosphonique.

La technique expérimentale de choix est la potentiométrie. Pour surmonter les difficultés rencontrées dans l'exploitation des données potentiométriques et pour améliorer leur interprétation, des méthodes de détermination, modifiées ou nouvelles, ont été introduites. Leur description a fait l'objet de deux articles précédents.[18,19]

PARTIE EXPERIMENTALE

Acides phosphoniques et réactifs

Les acides (méthyl-, éthyl-, chlorométhyl-, dichlorométhyl-) phosphoniques sont obtenus par hydrolyse, dans le tétrachlorure de carbone, des chlorures d'acides $RP(O)Cl_2$ correspondants; ceux-ci sont préparés par la méthode de Clay[20] et Kinnear et Perren,[21] excepté pour $ClCH_2P(O)Cl_2$ qui est préparé d'après Schwarzenbach *et al.*[22] La généralisation de la méthode de Kinnear et Perren[21] a permis la préparation des dibromures $BrCH_2P(O)Br_2$, $Br_2CHP(O)Br_2$ et $BrCH_2CH_2P(O)Br_2$ à partir de $AlBr_3$, PBr_3 et des bromures d'alkyle appropriés; comme Jonas et Schliebs[23] nous avons observé que l'utilisation du tribomure d'aluminium semble ne pas provo-

quer d'isomérisation de la chaîne carbonée. L'hydrolyse de ces composés aboutit aux acides (bromométhyl-, dibrométhyl-, bromo-2 éthyl-) phosphoniques. L'acide trichlorométhylphosphonique est préparé par la méthode de Kosolapoff.[24,25] L'acide hydroxyméthylphosphonique est obtenu par la méthode de Page.[26] L'acide iodométhylphosphonique provient de l'action de l'acide iodhydrique sur l'acide hydroxyméthylphosphonique selon Pitre et Grabitz.[27] L'acide triméthylammoniumméthylphosphonique est préparé par méthylation de l'aide *N,N*-diméthylaminométhylphosphonique à l'acide de l'iodure de méthyle en présence d'oxyde d'argent; il est isolé du mélange réactionnel par chromatographie sur résine échangeuse d'ions H^+ (Amberlite IR 120). L'analyse élémentaire de ces acides donne des résultats conformes à ceux attendus. Ces acides phosphoniques, souvent très hygroscopiques, sont difficilement purifiables. Cependant, l'acide méthylphosphonique est purifié aisément par recristallisations dans l'acétate d'éthyle, l'acide dibromométhylphosphonique est recristallisé dans le chlorure de méthylène. L'acide bromo-2 éthylphosphonique, de pureté satisfaisante est utilisé sans purification ultérieure. L'acide triméthylammoniumméthylphosphonique est reprécipité dans un mélange éthanol, acétate d'éthyle. L'acide iodométhylphosphonique est purifié à l'état de sel double $ICH_2PO_3H_2$, ICH_2PO_3HNa, modérément soluble dans l'eau. Tous les autres acides sont purifiés par l'intermédiaire de leurs sels monosodiques: une quantité équimolaire de soude est ajoutée à l'acide, le sel formé est généralement recristallisé en milieu eau–éthanol; seul $HOCH_2PO_3HNa$ requiert un minimum d'eau, un mélange d'eau et de dioxanne donne un très bon résultat pour l'obtention de Cl_3CPO_3HNa. La pureté de ces sels est déterminée par dosage pH-métrique. Tous les détails opératoires et les résultats des analyses sont développés par ailleurs.[28]

Les solutions stock des acides phosphoniques (acides méthyl-, dibromométhyl-, bromo-2 éthyl-, triméthylammoniumméthylphosphoniques exceptés) sont obtenues par passage de leur sel monosodique sur résine échangeuse de H^+ (Amberlite IR 120). Les solutions de nitrate de cuivre(II) et de nitrate de calcium(II) sont préparées à partir des produits de pureté garantie ($Cu(NO_3)_2$, $3H_2O$ et $Ca(NO_3)_2$, $4H_2O$ Merck *p.a.*). Leur dosage est effectué par échange d'ions sur résine Amberlite IR 120 (H^+) et détermination de l'acide fort ainsi libéré par la base forte utilisée pour les autres neutralisations. Le nitrate de potassium (Carlo-Erba RP-ACS) est utilisé sans purification ultérieure. Les solutions étalon d'acide chlorhydrique proviennent du passage de chlorure de potassium (Carlo-Erba, Standard primaire) sur résine échangeuse de H^+. La potasse titrante, dont le titre (0,1*M*) est proche de la concentration du sel de fond, est préparée par la méthode de Albert et Serjeant.[29] Malheureusement, dans nos conditions d'utilisation (reservoir couplé à une microburette) nous avons observé une légère carbonatation; lorsque celle-ci est stabilisée, des neutralisations d'acide chlornydrique permettent de calculer son titre. Tous ces dosages sont exploités par affinements multiparamétriques.

Ensemble de mesure

Tous les équilibres sont étudiés à 25,00 ± 0,05°; la température est maintenue constante à l'aide d'un circuit thermostaté, une cellule de titrage Tacussel RM O6 avec jaquette à circulation est utilisée. La solution à étudier est homogénéisée par agitation magnétique. Le passage d'un courant d'azote (purifié sur de la soude concentrée puis saturé en vapeur d'eau sur KNO_3 0,1*M* à 25°) au-dessus de la solution évite l'interférence du gaz carbonique extérieur. La potasse titrante est ajoutée à la microburette de 1 ml (résolution 0,005 ml; estimation à 0,001 ml près). Le pH expérimental est mesuré à l'aide d'un pH mètre-millivoltmètre PHM 64 Radiometer dont la résolution est de 0,001 unité de pH. La chaîne de mesure, constituée d'une électrode de verre (Ingold, type Lot 201 ou Schott, type U dans le cas des acides hydroxyméthyl- et triméthylammoniumméthylphosphoniques) et d'une électrode de référence au calomel (Ingold, type 303) est standardisée, avant chaque manipulation, à l'aide de tampons phtalate [pH(S) = 4,008] et borax [pH(S) = 9,180]. Il faut vérifier, en fin de titrage, que ces valeurs sont sensiblement inchangées. Pour un mélange donné, les neutralisations sont reprises jusqu'à reproductibilité satisfaisante qui correspond à résolution de l'appareillage.

Force ionique

Une force ionique μ de 0,100*M* est choisie. En effet, la littérature comporte nombre de constantes de stabilité déterminées dans les mêmes conditions: les comparaisons avec d'autres acides s'en trouveront facilitées. Le nitrate de potassium est utilisé. L'ion K^+ est imposé pour les neutralisations d'acides aminoalkylphosphoniques car il interfère faiblement sur la réponse de l'électrode de verre en milieu alcalin; l'ion nitrate est alors l'anion le plus satisfaisant, car à l'instar de l'ion perchlorate, il s'avère peu complexant.

Les acides phosphoniques seuls sont tous neutralisés en milieu 0,100*M* en KNO_3; la contribution à la force ionique des ions de l'acide est toujours négligée. Fixer la force ionique dans les études de complexes devient plus délicat. Dans les neutralisations de mélanges C_A, C_M, au lieu de maintenir la concentration de l'anion constante ($[NO_3^-] + 2C_M = 0{,}100M$), nous avons préféré fixer $[KNO_3] + 3C_M = 0{,}100M$ pour mieux tenir compte de la contribution du cation à la force ionique. En effet, pour les complexes peu stables (cas de Ca^{2+}), la forme libre du cation est prédominante. Bien que l'incidence de ce choix soit secondaire, nous pensons qu'il permet d'éviter au mieux la variation du pH par modification du coefficient d'activité.

Notons que la quantité initiale de KNO_3 est calculée pour atteindre la valeur choisie à la première équivalence car la majorité des déterminations s'effectuent à l'aide des données situées au delà de ce volume.

Etalonnages

Les données v, pH relatives au dosage de l'acide chlorhydrique par la potasse, en présence de KNO_3 0,100*M*, sont d'abord exploitées à l'aide du programme MUPROT, les équations de traitement sont celles correspondant à un système ouvert (expression 4).[18] En milieu acide fort, il est logique de considérer que la potasse se comporte comme si elle était exempte de carbonate ($C^*_{x1} = 0$). Par ajustement multiparamétrique on obtient les caractéristiques du réactif titrant ($H^0_x = -[K^+]_T$ et la concentration du carbonate en milieu basique C^*_{x2}) et les valeurs rattachées à la chaîne de mesure:

—avec l'électrode de verre Ingold, type Lot 201, la réponse s'écrit ($-\log h = -0{,}061 + \text{pH}$) avec $K_w = 1.9.10^{-14}$ pour $2 < \text{pH} < 10$; cette électrode n'étant pas prévue pour travailler en milieu basique.

—avec l'électrode Schott, type U, cette réponse devient ($-\log h = -0{,}069 + \text{pH}$) avec $K_w = 1{,}43.10^{-14}$ pour $2 < \text{pH} < 11{,}5$.

Les potentiels de jonction, négligeables, ne sont pas déterminables dans ces conditions.

Neutralisation des acides phosphoniques

La solution d'acide phosphonique ($4.10^{-3}M$), en milieu KNO_3 (0,100*M*), préparée par dilutions appropriées des solutions stock, est neutralisée par la potasse précédente. Les calculs sont menés comme suit. La réponse des électrodes, le produit ionique de l'eau et la concentration de la base forte H^0_x sont fixés. Dans tous les cas, la concentration en carbonate ajouté est toujours supposée nulle ($C^*_{x1} = 0$, expression 4)[18] dans la première partie de la courbe ($x < 1$, Fig. 1); seule la valeur de C^*_{x2} est affinée.

Suivant la nature de l'acide, les données utilisées appartiennent à des domaines différents de la courbe de neutralisation:

—pour les acides (méthyl- et éthyl-) phosphoniques, les deux constantes β_{021}, β_{011} ainsi que la concentration totale C_A^0 sont obtenues à partir des données allant jusqu'au second volume équivalent ($0 < x < 2$, Fig. 1).

—la première constante d'acidité des autres acides phosphoniques devenant de plus en plus forte est déterminée séparément par une technique spécifique aux acidités moyennement fortes;[30] elle est alors fixée dans les calculs. Seules les données de la seconde zone de pH sont utilisées ($1 < x < 2$, Fig. 1) et permettent d'obtenir β_{011} et C_A^0.

—dans le cas des acides (hydroxyméthyl- et triméthylammoniumméthyl-) phosphoniques, le produit ionique de l'eau est également ajusté en ajoutant les points de la région basique.

Formation des complexes

Les complexes sont étudiés par neutralisation de mélanges de cation (2.10^{-3} et $4.10^{-3}M$ pour Cu^{2+} et $4.10^{-3}M$ pour Ca^{2+}), d'acide phosphonique à la même concentration que précédemment ($4.10^{-3}M$) et de nitrate de potassium ($0.100 - 3\ C_M$)M, préparées à partir de solutions plus concentrées.

Le programme MUCOMP[19] est utilisé. On y fixe la réponse des électrodes. H_x^0, C_A^0, C_{x2}^*, K_W, β_{021} et β_{011} déterminés précédemment, ainsi que les constantes d'hydrolyse des cations (log $\beta_{2-20} = -10{,}7$ pour $Cu_2(OH)_2^{2+}$ et log $\beta_{1-10} = -12{,}9$ pour $CaOH^+$). En effet, comme le domaine d'existence des complexes est très restreint (voir Fig. 2), l'affinement multiparamétrique ne peut être employé à plein. Les points expérimentaux utilisés sont ceux compris entre la première zone d'équivalence et le début de précipitation (Fig. 2). Différents jeux de constantes de stabilité sont soumises à l'affinement; les espèces retenues sont celles qui sont affectées d'incertitudes acceptables et qui interprètent au mieux les données expérimentales (écart-type minimum).

RESULTATS ET DISCUSSION

Courbes de neutralisation

Les acides phosphoniques sont des diacides à fonctions séparées (Fig. 1); la première zone de pH ne présente pas de point d'inflexion ce qui est caractéristique d'un acide fortement ionisé à la concentration de l'étude. La neutralisation de la bétaïne $(CH_3)_3\overset{+}{N}CH_2PO_3H^-$ débuterait à $x = 1$; le tracé représenté sur la figure 1 correspond à la neutralisation d'un mélange équimolaire de cet acide et d'acide fort. L'acide bromo-2 éthylphosphonique constitue une exception: en effet, à partir de taux de neutralisation x voisins de 1, le pH décroît progressivement, le deuxième volume équivalent est reporté vers $x = 3$ indiquant une hydrolyse suivant:

$$BrCH_2CH_2PO_3^{2-} + H_2O \rightarrow HOCH_2CH_2PO_3^{2-} + H^+ + Br^-.$$

En conséquence, sa deuxième constante d'acidité ne peut être déterminée par affinement. Une valeur approximative a été estimée en extrapolant à des temps nuls le pH de différents mélanges.

La formation des complexes se traduit par un abaissement de pH par rapport à la courbe de neutralisation de l'acide seul (Fig. 2): la complexation est perceptible à partir de la première zone d'équivalence (domaine d'existence de RPO_3H^-/RPO_3^{2-}). Au vu des résultats du tableau 1, l'apparition des complexes s'accompagne d'un déplacement des protons ionisables par le cation (formation de RPO_3Cu, RPO_3Ca) ou d'une fixation d'ions hydroxyles (formation de $RPO_3Cu(OH)^-$).

Une précipitation est observée avec Cu(II). Dans le cas du système Cu(II)–acide chlorométhylphosphonique, différentes analyses (pH-métrique, complexométrique, élémentaire) indiquent la formation de $ClCH_2PO_3Cu.yCu(OH)_2$. Le phosphonate de cuivre $ClCH_2PO_3Cu$, peu soluble, évolue rapidement vers un phosphonate basique de cuivre. Suivant le pH de recueil du précipité, on trouve différentes valeurs de y ($y \sim 1$ pour pH ~ 7; $y \sim 4$ pour pH ~ 9). Tous les acides phosphoniques ont un comportement semblable. Cette précipitation simultanée ne permet pas d'isoler de composé bien défini; notons cependant qu'en opérant en milieu suffisamment acide, avec des solutions plus concentrées, on isole les formes RPO_3Cu hydratées. Le sel cuivrique de l'acide méthylphosphonique CH_3PO_3Cu est nettement moins soluble que les précédents comme le traduit la cassure sur la courbe de neutralisation. Cette forme prédomine et n'est transformée que lentement et à des pH élevés, en phosphonate basique.

Discussion

Les diverses constantes de stabilité

$$\beta_{qjp} = [M_qH_jA_p]/(m^qh^ja^p)$$

sont regroupées dans le tableau 1; y figurent également les constantes de formation successives $k_{qjp} = \beta_{qjp}/\beta_{q(j-1)p}$ qui sont équivalentes à l'inverse des constantes d'acidité (log $k_{021} = pK_1$; log $k_{011} =$ log $\beta_{011} = pK_2$).

L'incertitude sur les logβ_{qjp} est prise égale à $3\sigma_i/\beta_{qjp}$.ln 10) où σ_i est l'écart-type sur β_{qjp}; lorsque σ_i croît, cette évaluation est de plus en plus incorrecte et ne donne qu'une estimation grossière de l'erreur. Les constantes log k_{021}, relatives à première acidité, proviennent d'un mémoire antérieur;[30] l'incertitude, portée entre accolades { }, a été obtenue par le calcul d'erreur classique. Les constantes non affectées d'incertitude sont recalculées à partir des précédentes.

Les valeurs de log β_{011} sont en assez bon accord avec celles de la littérature, compte tenu des différences de force ionique (μ), de concentration (C_A) et de mode d'expression des constantes (constantes mixtes où l'activité de H^+ est introduite à la place de sa concentration). Les écarts importants observés sur log k_{021} sont dus aux méthodes trop sommaires qui y sont utilisées.

Dans un travail antérieur relatif à l'acide chlorométhylphosphonique,[17] nous avons calculé, par les méthodes classiques d'extrapolation, une constante relative à l'espèce CuA_2^{2-}; or celle-ci est nettement supplantée, suite à l'affinement, par $CuA(OH)^-$. Cette mauvaise interprétation a été rendue plausible parce

Tableau 1. Constantes de stabilité des acides phosphoniques H_2A et de leurs complexes de Ca^{2+} et Cu^{2+} .25° ; $\mu = 0{,}1 = [KNO_3] + 3C_M$

Acide	qjp	Espèce	log β_{qjp}	log k_{qjp}	Littérature: log β_{011}*; log k_{021}*
Trichlorométhylphosphonique	011	HA^-	4,477 (0,005)		4,81 ; 1,63 ($C_A = 0.005$)[25]
$Cl_3CPO_3H_2$	021	H_2A	$5{,}2_6$	$0{,}7_8$ {0,08}	4,930 ($\mu \rightarrow 0$)[31]
	101	CaA	1,25 (0,02)		
	101	CuA	2,17 (0,01)		
Triméthylammoniumméthyl-	011	HA	5,099 (0,003)		
phosphonique	101	CaA^+	0,93 (0,03)		
$(CH_3)_3\overset{+}{N}CH_2PO_3H_2$	101	CuA^+	2,180 (0,007)	$6{,}9_2$	
	1-11	Cu(OH)A	$-4{,}7_4$ (0,08)†		
Dichlorométhylphosphonique	011	HA^-	5,213 (0,003)		5,61 ; 1,14 ($C_A = 0.005$)[25]
$Cl_2CHPO_3H_2$	021	H_2A	5,9	0,7 {0,1}	5,604 ($\mu \rightarrow 0$)[31]
	101	CaA	1,26 (0,03)		
	101	CuA	2,490 (0,004)	$7{,}2_0$	
	1-11	Cu(OH)A	$-4{,}7_1$ (0,07)†		
Dibromométhylphosphonique	011	HA^-	5,40 (0,01)		
$Br_2CHPO_3H_2$	021	H_2A	6,2 ($0{,}1_5$)	0,8	
Chlorométhylphosphonique	011	HA^-	6,169 (0,006)		6,30 ; 1,40 ($C_A = 0.005$)[25]
$ClCH_2PO_3H_2$	021	H_2A	7,21	1,04 {0,05}	6,17 ; 1,51 ($\mu = 0{,}1$)[1]
					6,588 ($\mu \rightarrow 0$)[31]
	101	CaA	1,38 (0,02)		
	101	CuA	2,89 (0,02)	6,62	
	1-11	$Cu(OH)A^-$	−3,73 (0,03)		
	102	CuA_2^{2-}	‡		
Bromométhylphosphonique	011	HA^-	6,235 (0,004)		6,52 ; 1,14 ($C_A = 0.005$)[25]
$BrCH_2PO_3H_2$	021	H_2A	7,38	1,15 {0,04}	
	101	CaA	1,34 (0,03)		
	101	CuA	2,951 (0,006)	6,86	
	1-11	$Cu(OH)A^-$	−3,91 (0,01)		

Iodométhylphosphonique $ICH_2PO_3H_2$	011	HA^-	6,435 (0,004)		6,72; 1,30 ($C_A = 0,005$)[25]
	021	H_2A	7,70	1,27 {0,04}	
	101	CaA	1,37 (0,03)		
	101	CuA	3,04 (0,01)	6,76	
	1-11	$Cu(OH)A^-$	−3,72 (0,03)		
Bromo-2 éthylphosphonique $BrCH_2CH_2PO_3H_2$	011	HA^-	6,9§		
	021	H_2A		1,62 {0,02}	
Hydroxyméthylphosphonique $HOCH_2PO_3H_2$	011	HA^-	6,970 (0,005)		7,15; 1,91 ($C_A = 0,005$)[25]
	021	H_2A	8,67	1,70 {0,02}	7,90; 1,79 ($\mu \rightarrow 0$)[3]
					7,364 ($\mu \rightarrow 0$)[31]
	101	CaA	1,68 (0,01)		
	101	CuA	3,53 (0,05)	$6,1_8$	
	1-11	$Cu(OH)A^-$	−2,65 (0,08)		
Méthylphosphonique $CH_3PO_3H_2$	011	HA^-	7,547 (0,004)		7,76; 2,33[32]
	021	H_2A	9,737 (0,007)	2,19	7,1; 2,35 ($C_A = 0,1$)[33]
					7,34; 2,48 ($C_A = 0,05$)[34]
					7,74; 2,38 ($C_A = 0,005$)[35]
					7,35; 2,41 ($\mu = 0,1$)[1]
					7,29; 2,12 ($\mu = 0,2$)[2]
					8,000 ($\mu \rightarrow 0$)[31]
	101	CaA	1,51 (0,02)		
	101	CuA	3,52 (0,04)	6,9	
	1-11	$Cu(OH)A^-$	−3,4 (0,3)		
Éthylphosphonique $C_2H_5PO_3H_2$	011	HA^-	7,794 (0,004)		7,98; 2,39[32]
	021	H_2A	10,084 (0,007)	2,29	7,85; 2,45 ($C_A = 0,1$)[33]
					8,05; 2,43 ($C_A = 0,005$)[35]
	101	CaA	1,54 (0,02)		
	101	CuA	3,59 (0,04)	6,56	
	1-11	$Cu(OH)A^-$	−2,97 (0,06)		

Remarques: * Constantes mixtes, sauf pour $\mu \rightarrow 0$.
† Constante fortement tributaire de $Cu_2(OH)_2^{2+}$.
‡ La présence de CuA_2^{2-} a été décelée, mais ne peut être retenue, car l'incertitude est trop importante ($3\sigma \sim \beta_{102}$).
§ Valeur extrapolée, l'acide se décomposant en $HOCH_2CH_2PO_3H_2$.

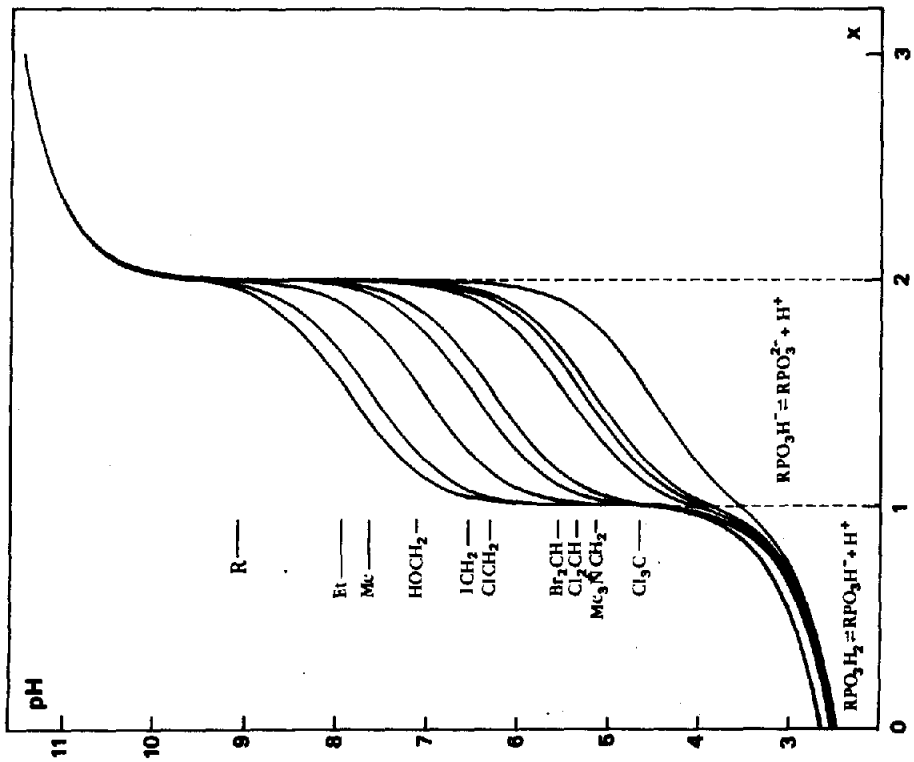

Fig. 1. Courbes de neutralisation d'acides phosphoniques RPO_3H_2 ($C_A^0 = 4.17.10^{-3} M$; $v_0 = 48$ ml; H_x^0 *ca.* $-0.1 M$). Influence des substituants sur l'acidité.

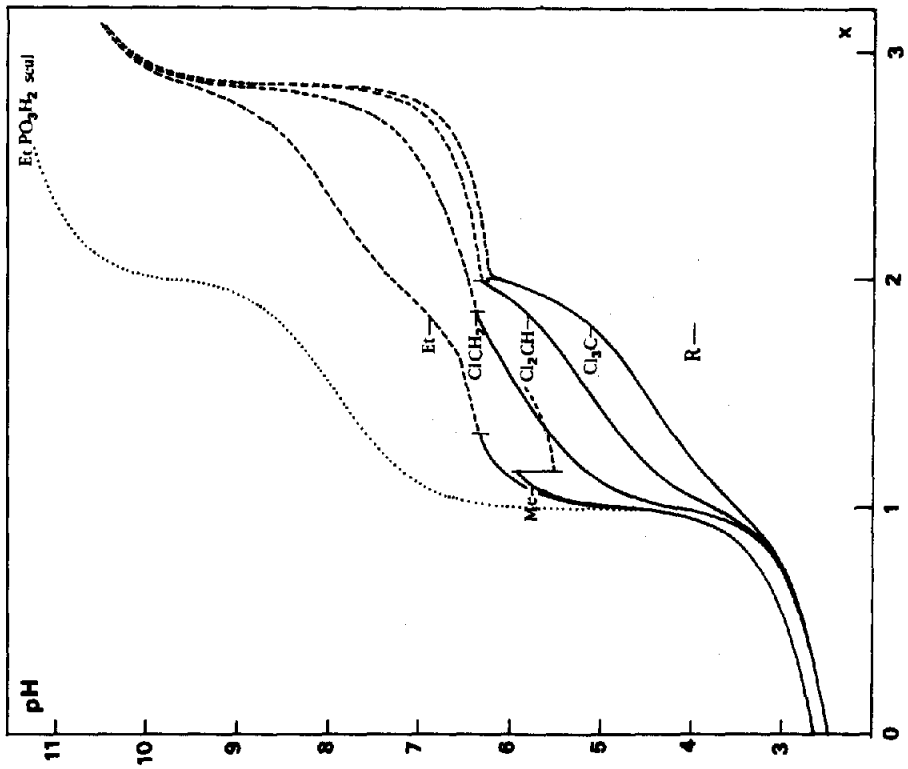

Fig. 2. Courbes de neutralisation de mélanges d'acide phosphonique RPO_3H_2 et de cuivre(II) ($C_A^0 = 4.17.10^{-3} M$; C_X^0/C_M^0 *ca.* 2; $v_0 = 48$ ml; H_x^0 *ca.* $-0.1 M$). --- précipitation (zone hors équilibre).

que les formations de CuA_2^{2-} et de $CuA(OH)^-$ libèrent le même nombre de protons ($Cu^{2+} + 2HA^- \rightleftharpoons CuA_2^{2-} + 2H^+$ et $Cu^{2+} + HA^- + H_2O \rightleftharpoons CuA(OH)^- + 2H^+$) et que les graphes ne présentent pas de critère suffisamment net pour rejeter cette hypothèse.

L'existence de l'espèce $CH_3PO_3Cu(OH)^-$ est douteuse car le domaine de confiance 3σ est assez élevé: ceci est cohérent avec l'absence, dans le cas de cet acide, du précipité de phosphonate basique.

Certains auteurs ont annoncé une mobilité importante de l'hydrogène du groupement hydroxyle de l'acide hydroxyméthylphosphonique.[36,37] Or les résultats de l'affinement excluent l'existence de cette acidité puisque le produit ionique de l'eau est fidèlement retrouvé. L'affinement multiparamétrique, en envisageant tous les paramètres (impuretés, réponse des électrodes...) évite de se méprendre. Dans le cas de l'acide triméthylammoniumméthylphosphonique, K_w a également la valeur attendue, ce qui permet de vérifier que le groupement $(CH_3)_3\overset{+}{N}-$ n'a aucune interaction avec les ions hydroxyles.

La figure 3, qui comporte les tracés $\log \beta_{101} = f(\log \beta_{011})$, traduit la répercussion de l'acidité du groupement phosphonique ($-PO_3^{2-} + H^+ \rightleftharpoons -PO_3H^-$) ($\log \beta_{011}$) sur son pouvoir complexant ($-PO_3^{2-} + M^{2+} \rightleftharpoons -PO_3M$) ($\log \beta_{101}$) vis à vis de Ca^{2+} et Cu^{2+}. Toutes les valeurs représentatives des différents acides, à l'exception des acides hydroxyméthylphosphonique et triméthylammoniumméthylphosphonique, se situent sur une droite. Les complexes de Ca^{2+} sont peu stables, cette stabilité n'est que très légèrement favorisée par une diminution de l'acidité de $-PO_3H^-$, ce que traduit l'équation de la droite: $\log \beta_{101} = 0{,}80 + 0{,}09_2 \log \beta_{011}$. Par contre, pour les complexes de Cu^{2+} on obtient $\log \beta_{101} = 0{,}23 + 0{,}434 \log \beta_{011}$, le pouvoir complexant étant plus sensible à l'acidité. Les anions $HOCH_2PO_3^{2-}$ et $(CH_3)_3\overset{+}{N}CH_2PO_3^{2-}$ doivent complexer de manière différente car leurs points représentatifs se situent en dehors des droites. Le regain de stabilité des hydroxyméthylphosphonates provient certainement de la stabilisation du complexe par formation d'un cycle à

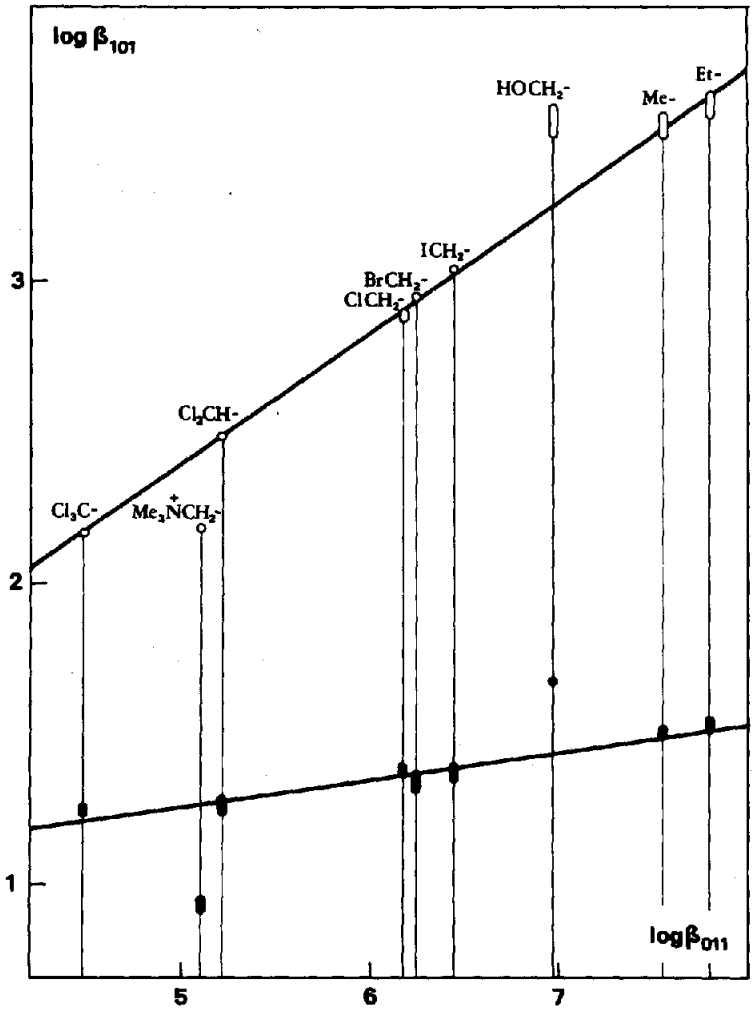

Fig. 3. Influence de l'acidité $\log \beta_{011}$ du groupement phosphonique sur la stabilité $\log \beta_{101}$ des complexes du calcium(II) [●] et du cuivre(II) [○].

cinq chaînons où entre l'oxygène du groupement hydroxyle. Les espèces formées à partir du triméthylammoniumméthylphosphonate présentent au contraire un défaut de stabilité. Ceci est logique, car ce ligand n'a plus globalement qu'une seule charge négative; en d'autres termes, la stabilité moindre est due à la répulsion entre le cation et $(CH_3)_3\overset{+}{N}-$. Ce comportement préfigure celui des acides aminoalkylphosphoniques $>\overset{+}{N}H(R)PO_3^{2-}$ comprenant un ammonium non dissocié.

Nous pouvons donc conclure que le pouvoir complexant du groupement phosphonique dépend linéairement de son acidité, les exceptions rencontrées étant aisément explicables. Ces résultats seront utilisés par la suite dans l'interprétation des propriétés des acides aminoalkylphosphoniques.

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Summary—The stability constants of some phosphonic acids RPO_3H_2 [R = CH_3, C_2H_5, $ClCH_2$, Cl_2CH, Cl_3C, $BrCH_2$, Br_2CH, $BrCH_2CH_2$, ICH_2, $HOCH_2$, $(CH_3)_3\overset{+}{N}CH_2$] and their complexes RPO_3Ca, RPO_3Cu, $RPO_3Cu(OH)^-$ have been determined by multiparametric refinement of potentiometric titration data obtained at 25°, in a 0.1*M* potassium nitrate medium. Linear relationships are obtained between stability and acidity constants. Formation of five-membered rings stabilize the hydroxymethylphosphonates. Conversely, cation repulsion by the permanent positive charge reduces the stabilities of complexes with trimethylammoniummethylphosphonic acid.

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AN EVALUATION OF METHODS OF ANALYSIS FOR ALKYLAMINO-OXOMETHANESULPHATES

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Summary—Three possible ways of determining univalent cation salts of alkylamino-oxomethanesulphonic acids, R–NHCOSO$_3^-$M$^+$, were examined. Of these methods (gravimetric determination as the urea, as barium sulphate, or by an iodometric method), the iodometric method of estimating the bisulphite liberated from alkylamino-oxomethanesulphonates by decomposition with sodium hydroxide was finally selected and evaluated. Results obtained are in good agreement with theory for R = butyl and R = –(CH$_2$)$_6$–. The iodometric method was equally applicable to polyurethane precursors. Free or excess of bisulphite (and accordingly total bisulphite) was determined successfully in the case of the polymeric adduct.

Our interest in poly(carbamoyl sulphonates) (PCS)*, prepared according to equation (1),

$$\text{R–NCO} + \text{HSO}_3^- \rightarrow \text{R–NHCOSO}_3^- \qquad (1)$$

has caused us to examine various possible methods of analysis for the reactive group. Analytical techniques could be based upon various reactions of carbamoyl sulphonates; for example, nucleophilic attack by hydroxyl ion or primary or secondary amines, or estimation of the bisulphite† liberated by such nucleophilic reactions. We selected three possible analytical methods based upon these reactions for examination in detail, using model compounds, and then assessed the utility of the methods for the analysis of PCS. Because polymers are generally a complex mixture of species, they present problems in comparison with model compounds and only one of the analytical methods proved satisfactory for use with the polymers.

The three methods selected were: (*A*) precipitation as *N*,*N*′-disubstituted ureas by reaction with primary amines, (*B*) liberation of bisulphite by nucleophilic attack with hydroxyl ion, oxidation of this liberated bisulphite and gravimetric determination as barium sulphate, and (*C*) liberation of the bisulphite by reaction with hydroxide and determination by iodometry. Methods *B* and *C* have the advantage that the amount of free bisulphite can also be determined (*i.e.*, that bisulphite which is not in combined form as the carbamoyl sulphonate). The iodometric method was shown to be most suitable for analysis of alkylamino-oxomethanesulphonates and this paper presents an evaluation of the accuracy and reproducibility of the various methods.

* Correctly termed poly(alkylamino-oxomethanesulphonates); these are water-soluble and water-stable derivatives of telechelic isocyanate prepolymers.[1,2]

† Bisulphite refers to bisulphite (HSO_3^-) and other sulphite species (SO_3^{2-}, $S_2O_5^{2-}$) in solution; disulphite refers specifically to $S_2O_5^{2-}$ as the solid.

EXPERIMENTAL

Reagents

Sodium thiosulphate (0.1*N*), iodine (0.1*N*), sodium hydroxide (0.2*M*) and hydrochloric acid (2.0*M*) were all prepared from commercially available concentrated solutions; all except the sodium thiosulphate were prepared in 50% v/v propanol/water; the thiosulphate was prepared in demineralized water. The iodine and thiosulphate solutions were standardized with potassium iodate.[3] Potassium iodide solution (10%, pH 8) was prepared with demineralized water. The sole function of the propanol was to maintain a homogeneous solution, and propan-1-ol and propan-2-ol were used interchangeably.

The sodium disulphite (laboratory reagent grade)† was 95.1% pure as determined by iodometric analysis.[3,4] The potassium disulphite (analytical reagent grade) was not assayed, as derivatives prepared from it were recrystallized several times.

1,6-Di-isocyanatohexane was fractionally distilled (b.p. 92–96°/1 mmHg) before use. Butyl isocyanate was used as supplied. All other chemicals were analytical grade or equivalent and were employed without further purification.

Preparation of model compounds

Bisulphite adducts of butyl isocyanate and 1,6-di-isocyanatohexane. The potassium bisulfite adducts were prepared as described in the literature,[2] except that ethanol was used instead of dioxan in preparation of the adduct from 1,6-di-isocyanatohexane. These carbamoyl sulphonates are denoted by BuNCO/$KHSO_3$ and HDI/$KHSO_3$ respectively.

The BuNCO/$KHSO_3$ was purified first by ethanol precipitation from aqueous solution at room temperature and collection of the central 80% (approximately) cut of precipitate, and then by crystallization from a saturated solution in water at room temperature by cooling to 4°. The purified material was dried *in vacuo* over phosphorus pentoxide at room temperature and used almost immediately. (Found: C, 27.5%; H, 4.7%; N, 6.7%; S, 14.5%; sulphated ash at 800°, 40.2%. $C_5H_{10}NO_4SK$ requires C, 27.38%; H, 4.60%; N, 6.39%; S, 14.62%; K_2SO_4, 39.73%.)

The $HDI/KHSO_3$ was purified similarly but three ethanol precipitations and three crystallizations from water were performed to ensure maximum purity. (Found: C, 23.7%; H, 3.6%; N, 6.9%; S, 15.5%; sulphated ash at 800°, 42.5%. $C_8H_{14}N_2O_8S_2K_2$ requires C, 23.52%; H, 3.45%; N, 6.86%; S, 15.70%; K_2SO_4, 42.64%.) The melting temperature of both $BuNCO/KHSO_3$ and $HDI/KHSO_3$ exceeds 300° and was therefore not used as a criterion of purity.

Bisulfite adduct of prepolymer A. Prepolymer A is a commercial polymer containing terminal aliphatic isocyanate groups. The polymer is trifunctional, having a molecular weight of about 3500 with a poly(propylene oxide) backbone; analysis of our sample gave solids (*i.e.*, non-volatiles) content 85.5%, isocyanate content 3.0%; the diluent solvent was ethyl acetate.

The bisulphite adduct was typically prepared as follows to give a homogeneous solution: to 100 g of prepolymer A, vigorously stirred in a flask flushed with nitrogen, was added a solution of 8.0 g of sodium disulphite (*i.e.*, 18% excess over the stoichiometric amount) in 75.4 g of water and 180.9 g of ethanol. The initial cloudy dispersion rapidly went clear (5 min), but was stirred for a total of 1 hr. This is a modification of a method employed previously for a similar polymer.[2] A weighed amount of the resulting homogeneous solution was diluted appropriately for bisulphite determination.

Analytical methods

(*A*) *Analysis by precipitation as dialkyl urea.* The carbamoyl sulphonate (10 meq) was dissolved in water (20–40 ml, depending on the solubility) at room temperature and the amine added with gentle agitation. The mixture was stood at room temperature for 2 hr, and then at 4° overnight. The precipitate was filtered off on a porosity-4 sintered-glass crucible, washed with six 10-ml portions of water at 4° and dried to constant weight at reduced pressure (1 mmHg) over phosphorus pentoxide at room temperature.

(*B*) *Gravimetric analysis as barium sulphate.* The carbamoyl sulphonate (10 meq) was dissolved in demineralized water (250 ml). To a 25.0-ml aliquot were added 50 ml of 0.4*M* sodium hydroxide and the mixture was allowed to react for 20 min before being made slightly acid with 1*M* hydrochloric acid. Two ml of hydrogen peroxide (100-vol) were then added; after 10 min, gentle heating was started and 25 ml of 1*M* hydrochloric acid were added together with water to give a total volume of 400 ml. When the solution was almost boiling, 100 ml of hot 1% barium chloride solution were added rapidly with stirring. The precipitate was digested overnight on a steam-bath, filtered off on a Whatman No. 542 paper and, after thorough washing, ignited at 800–900° for 1 hr, cooled and weighed.

(*C*) *Iodometric analysis.* A sample containing a total of about 1.5 g of $KHSO_3$ (including combined and free bisulphite) was dissolved in demineralized water (500 ml). A 25.0-ml aliquot of the solution was transferred to an iodine flask, 50 ml of 0.2*M* sodium hydroxide were added, followed by 100 ml of 50% v/v propanol/water; after flushing of the flask with a stream of nitrogen for 15 sec, the solution was allowed to stand in the stoppered flask for 10 min at room temperature.

To the flask were added rapidly 15 ml of 2*M* hydrochloric acid, 25.0 ml of 0.1*N* iodine and 10 ml of 10% potassium iodide solution. The flask was allowed to stand for 5 min in the dark, and then its contents were titrated with standardized 0.1*N* sodium thiosulphate. Starch could not be used as an indicator because of the propanol present and the end-point was indicated by the disappearance of the yellow colour of iodine which, with care, could be observed with an error of only ± 0.02 ml.

A blank titration was done by following the same procedure but without sample. The free bisulphite was obtained by following the procedure without addition of the sodium hydroxide.

This standard procedure was varied in the following ways:

(*i*) Effect of EDTA. The sample of adduct was dissolved in 0.001*M* or 0.025*M* EDTA (disodium salt) instead of demineralized water; otherwise the determination was performed as above.

(*ii*) Reversal of order of mixing the sample and iodine solutions. A sample containing the equivalent of 3 g of $KHSO_3$ was dissolved in water (500 ml). A 25.0-ml aliquot was transferred to a 100-ml standard flask, 50 ml of 0.4*N* sodium hydroxide (dissolved in propanol/water) were added and the flask was flushed with nitrogen; after 10 min, 15 ml of 4*M* hydrochloric acid (in propanol/water) were added and the contents diluted accurately to 100 ml with 50% v/v propanol/water. A 50.0-ml aliquot was transferred to an iodine flask containing 25.0 ml of 0.1*N* iodine plus 65 ml of 50% v/v propanol/water and 10 ml of potassium iodide solution were added. The sample was titrated as before.

(*iii*) Adduct of prepolymer A. The sample was diluted with water. The polymeric urea produced by decomposition of the adduct sometimes precipitates, but redissolves on addition of neat propanol. This addition of extra propanol causes no change in the observed result but permits much easier detection of the end-point.

RESULTS AND DISCUSSION

Several possible methods of analysing carbamoyl sulphonates are indicated from an examination of the chemistry of nucleophilic attack on the carbamoyl sulphonate [equation (2)].

$$R\text{–}NH\text{–}CO\text{–}SO_3^- + BH \rightarrow R\text{–}NH\text{–}CO\text{–}B + HSO_3^- \quad (2)$$

If a base such as hydroxyl ion or RNH_2 were used, consumption of the base could be determined but the bisulphite concomitantly liberated would consume an indeterminable amount of base, rendering the procedure unsatisfactory. A primary amine, however, would also produce a relatively insoluble *N,N'*-disubstituted urea which could be determined gravimetrically (method *A*) although, for polymers, the increased solubility conferred on the urea by the polymeric backbone might be a problem.

Attack by hydroxyl ion on the carbamoyl sulphonate can be employed as the basis for two other analytical methods: oxidation of the liberated bisulphite to sulphate and its determination as barium sulphate (method *B*), or iodometric determination of the liberated bisulphite (method *C*).

A. Analysis by precipitation as N,N-*disubstituted urea.* When $BuNCO/KHSO_3$ and $HDI/KHSO_3$ were reacted with 95–300% of the stoichiometric quantity of butylamine and benzylamine, weights of ureas corresponding to 47–112% of the theoretical yield were obtained. The low yields may have been due to insufficient amine having been present; high yields are unlikely to be caused by excess of amine or amine carbonate (from reaction with atmospheric CO_2) as these compounds have good solubility in water. On the other hand, the ureas were found to have low

solubility in water (<0.4% at 4°) and should have been quantitatively precipitated.

By performing 4 or 5 separate determinations of each of the 4 possible combinations of carbamoyl sulphate and amine, and by using standardized precipitation conditions, we observed: (1) that the yield of each urea was self-consistent, (2) that HDI/$KHSO_3$ consistently gave higher yields of urea than did BuNCO/$KHSO_3$ whereas iodometric analysis indicated they were of comparable purity and (3) that benzyl ureas consistently gave higher yields than butyl ureas. Additionally, the precipitates were difficult to filter off and dry (requiring 7 days at 1 mm Hg over phosphorus pentoxide before attaining constant weight). Irrespective of their causes, these problems were considered sufficient to render the method unsuitable for use with polymers. A further limitation of the method is that it provides only a value for the carbamoyl sulphonate.

B. Analysis by liberation of bisulphite and its estimation as sulphate. For polymeric samples this method offers the advantage that it is capable of determining both free bisulphite plus bisulphate as well as carbamoyl sulphonate, because the carbamoyl sulphonate is not decomposed by hydrogen peroxide. (Solutions of pure carbamoyl sulphonate salts precipitate no barium sulphate after addition of barium chloride and hydrogen peroxide, even after heating to the boil.[5])

Results obtained by this method show reasonable precision but not accuracy. The values found for carbamoyl sulphonate content from a series of 14 tests were generally 0.5–2% high; on re-ignition after the addition of 1 or 2 drops of sulphuric acid to the barium sulphate precipitate, a further 0.5–1% increase was observed. These high results indicate the presence of occluded or co-precipitated salts, this having occurred despite careful attention to precipitation and digestion of the precipitate so as to minimize these effects.

On application of this method to a PCS prepared from prepolymer A, the carbamoyl sulphonate content found was 70% high. Additional problems were encountered with the large sample size, necessitated by the low sulphur content of the polymer, and with precipitation of polymer, which was insoluble in the aqueous organic solvent. While this method is unsuited to the determination of carbamoyl sulphonate content, it may be of value for determining free bisulphite plus bisulphate in concentrated PCS solutions, for which sample volumes can be kept small.

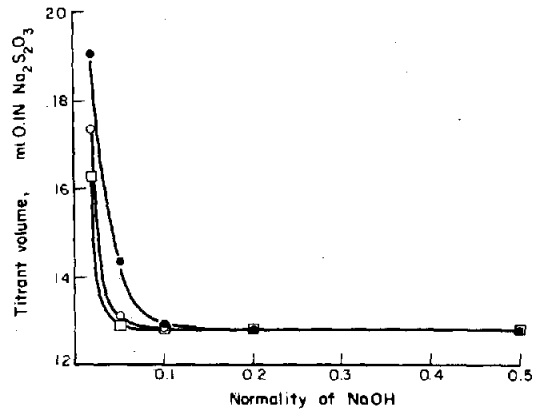

Fig. 1. Effects of time of treatment and concentration of NaOH on decomposition of BuNCO/$KHSO_3$ (not flushed with nitrogen). Time of treatment: ● 5 min; ○ 10 min; □ 20 min.

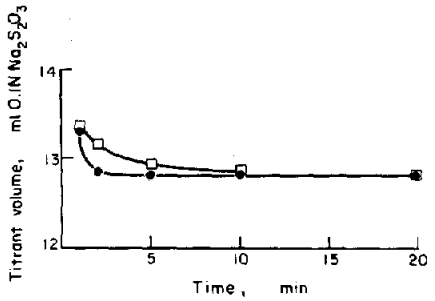

Fig. 2. Effect of nitrogen flushing on the reaction rate of BuNCO/$KHSO_3$ with 0.1*M* NaOH: ● flushed; □ not flushed.

C. Iodometric analysis. Sodium hydroxide was used to decompose the carbamoyl sulphonate, and the effects of alkali concentration, nitrogen flushing and the time allowed for decomposition were investigated: results for these three factors are given in Figs. 1 and 2. When the alkali concentration was varied, different amounts of hydrochloric acid were added in order to maintain a constant final acidity.

From Fig. 1 it can be seen that if the decomposition is allowed to proceed for only 5 min, a sodium hydroxide concentration of 0.2*M* is necessary to decompose the carbamoyl sulphonate completely, but when a period of 10 or 20 min is employed, 0.1*M* alkali is sufficient. With 0.02*M* sodium hydroxide complete decomposition is not achieved even after 19 hr. Although the 0.02*M* alkali provides 3 times the stoichiometric quantity of hydroxide necessary for this decomposition under the conditions used, it does not maintain a sufficiently high solution pH for the reaction to proceed at a reasonable rate, because of the mild acidity of the liberated bisulphite.

When 0.2*M* sodium hydroxide is employed, between 2 and 5 min is sufficient time to effect complete decomposition of the carbamoyl sulphonate (Fig. 2), but the resulting titration value (and hence the amount of bisulphite determined) depends upon whether the system is flushed with nitrogen. Nitrogen flushing reduces aerial oxidation of the liberated bisulphite and one flushing appears to be advantageous; a second flushing produces only a marginal improvement in results (Table 1). The nitrogen flushing also appears to prevent the retardation of decomposition of the carbamoyl sulphonate observed in the presence of air, because the time needed to reach an equilibrium titration value after flushing with nitrogen is half that observed when the flushing is omitted.

Table 1. Effect of N_2 flushing on determination of $KHSO_3$ released from $BuNCO/KHSO_3$ by NaOH

Sample*	0.1*N* thiosulphate used, *ml*†
1	12.85
2	12.80
3	12.78

* Sample 1: standard method, but no flush with nitrogen. Sample 2: as for 1, but flask flushed for 15 sec with a stream of nitrogen after addition of the 0.2*M* NaOH to the sample aliquot.

Sample 3: as for 2, but flask also flushed for 15 sec with a stream of nitrogen after addition of the 0.1*N* iodine.

† Means of 3 determinations.

Table 3. Accuracy and precision of results: repeated estimates of the $KHSO_3$ content of $BuNCO/KHSO_3$ and $HDI/KHSO_3$ by the standardized method

Run	Mean %	Std. devn., %	Replicates Blanks	Samples
$BuNCO/KHSO_3$				
1	54.81	0.009	5	8
2	54.73	0.003	3	8
3	54.65	0.005	3	8
4	54.81	0.005	3	4
Theoretical value	54.80			
$HDI/KHSO_3$	58.61	0.007	5	7
Theoretical value	58.83			

If oxidation were the sole difference between the samples, then equilibrium should be approached at approximately the same rate in each case but the titration value would be higher for the non-flushed example, thus giving a lower apparent carbamoyl sulphonate content, due to loss by oxidation. Nitrogen flushing was therefore adopted as part of the standard analytical procedure.

Humphrey *et al.*[6] employed 0.001*M* EDTA to stabilize 0.001*M* sodium sulphite. Our solutions of $BuNCO/KHSO_3$ were 0.025*M* (with respect to available bisulphite) and we therefore investigated the use of EDTA at both concentrations. The results (Table 2) show that EDTA has a slightly deleterious effect on the analysis. It is also apparent that 0.001*M* EDTA has almost as great an effect as does 0.025*M* EDTA. Since EDTA leads to inferior results, its use was discontinued.

It is asserted[3,4] that the best method of analysis of sulphite solutions is to add the sulphite slowly to the iodine solution with the tip of the pipette near the surface of the iodine solution. We therefore examined the effect of adding the solution of decomposed adduct to the iodine solution. It was found that this order of addition was more tedious and gave results which were less accurate and precise than those obtained by our standard method. Thus the method as developed was preferred.

To summarize, the method described works adequately, and the high accuracy and precision of the results can be observed from Table 3. The mean values presented in Table 3 for the separate runs of $BuNCO/KHSO_3$ differ significantly, however, and this is attributed to an aging effect. Runs 1–3 were separate determinations performed on the same batch of $BuNCO/KHSO_3$ on successive days. Run 4 was the initial determination on a freshly prepared batch of the material and the agreement between runs 1 and 4 is obvious. The experimental value is in acceptable agreement with the theoretical value for $HDI/KHSO_3$.

Table 2. Effect of EDTA on determination of $KHSO_3$ released from $BuNCO/KHSO_3$ by 0.2*M* NaOH

Solvent for $BuNCO/KHSO_3$ sample	Demineralized water	0.001*M* EDTA	0.025*M* EDTA
g of $KHSO_3$/100 g of adduct*	54.79†	54.59§	54.55‡

* Mean values given: theoretical value 54.80.

† 8 Replicates of sample titration, 5 replicates of blank titration.

§ 4 Replicates of sample titration, 3 replicates of blank titration.

‡ 5 Replicates of sample titration, 3 replicates of blank titration.

Our interest is primarily in the assessment of analytical methods for telechelic polymers terminated with carbamoyl sulphonates, but as model compounds are far more satisfactory than a prepolymer for evaluation purposes, only a single result for the prepolymer will be presented here. Detailed results arising from the application of the method to prepolymer studies will be published elsewhere.[7]

In normal preparation of the bisulphite adduct of prepolymer A, a 10–20% excess of sodium bisulphite is used. This excess is employed to allow for the lower degree of purity of the sodium disulphite *vis-à-vis* the potassium salt, to allow for oxidative losses of HSO_3^- during preparation and storage of the adduct, and to reduce the possibility of side-reactions (especially reaction of the isocyanate groups with ethanol or water). Thus with the bisulphite adduct of prepolymer A, unlike the situation with the easily recrystallizable model compounds, excess of bisulphite will be present in the homogeneous product system, and some of it will be oxidized to sulphate. The sum of the experimentally determined combined and free bisulphite can therefore be expected to be somewhat less than the amount of sodium disulphite (expressed as the hydrated product, sodium bisulphite) used in the preparation of the adduct.

Table 4 sets out the analytical results for the bisulphite adduct of prepolymer A, together with the values calculated from the appropriate data. From the agreement between the experimental and calculated results, the usefulness of the analytical method developed is apparent, and it can be seen that over 99% of the isocyanate groups have reacted with sodium bisulphite under the conditions used. The low value for free bisulphite reflects probable oxidative

Table 4. Analysis of the carbamoyl sulphonate content of a bisulphite adduct of prepolymer A

	Experimental values*	Theoretical values*
Combined hydrogen sulphite	8.75 ± 0.09†	8.80
Free hydrogen sulphite	1.06 ± 0.05	1.62
Total hydrogen sulphite	9.81 ± 0.04	10.41

* All values expressed as g of $NaHSO_3$ present in a solution containing 100 g of non-volatiles (*i.e.*, hydrogen sulphite adduct of prepolymer A + excess of inorganic salts).
† Standard deviation, based on 4 replicate determinations.

loss as sulphate, or perhaps some slight loss of gaseous SO_2 from the system: these losses are also apparent in the determination of total bisulphite.

Sources of error

Provided the procedures described are followed carefully, it is evident from the results presented (especially in Tables 3 and 4) that accurate, precise and reliable analyses can be performed. However, a brief discussion of some of the possible sources of error is appropriate because of the precautions that must be taken.

First, as the determination is a back-titration method, the results are very sensitive to errors in the blank titration because its mean value is used in all calculations. As the difference in titration volumes is used for the calculation of each result, the errors are additive.

Secondly, we must consider the purity of the sample itself: Guise *et al.*[2] found that their sample of BuNCO/$KHSO_3$ was more than 90% pure according to estimation of the isocyanate available to dibutylamine, and that no free bisulphite could be detected with iodine. They noted, however, that it was not possible to remove small amounts of excess of potassium sulphite from potassium ethylamino-oxomethanesulphonate: presumably the ethyl derivative is too similar in solubility to potassium sulphite/bisulphite, whereas the butyl derivative differs markedly in solubility because of the effects of the larger alkyl group. In view of these observations, the BuNCO/$KHSO_3$ was carefully recrystallized by two different techniques. The chief impurities were likely to be potassium sulphite, bisulphite, sulphate, bisulphate and dibutyl urea: of these, potassium sulphite or bisulphite would lead to erroneously high values; the various other impurities can be regarded as inert, leading to erroneously low values.

With the BuNCO/$KHSO_3$ and HDI/$KHSO_3$ used in this work, no change in the infrared spectra was observed for either compound after the first precipitation step during purification. The compounds were shown to be free from sulphite species, by the absence of reducing properties towards dilute iodine solution. Any ureas or urethanes present should have been removed in the ethanol precipitation steps, owing to their solubilities being higher in ethanol than in water.

Thirdly, errors could arise from oxidation or loss of liberated bisulphite. It was hoped to reduce this risk of oxidation by flushing with nitrogen. On acidification, there could be some loss of SO_2, due to conversion of HSO_3^- into sulphurous acid: it was hoped that this loss would be minimized by prompt addition of the iodine solution, and by restriction of the degree of acidification. The results indicate that, with these precautions, loss of SO_2 is minimal and that this method of estimating sulphite species is both accurate and reproducible.

Fourthly, we considered the order of mixing of the reactants, either iodine to the bisulphite solution, or the more generally accepted[3,4] reverse order. We showed that the first order of addition gave the more satisfactory results, mainly, we believe, because the use of nitrogen flushing decreases oxidation of the bisulphite.

Acknowledgements—We wish to thank G. B. Guise and M. Rushforth for providing information on the basic iodometric test method. Thanks are also due to Bayer A. G. for samples of Desmodur H. In particular, we are indebted to Miss S. A. Y. Smith for competent technical assistance.

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EXTRACTION OF METAL IONS FROM CHLORIDE SOLUTION WITH *N,N*-DIOCTYLACETAMIDE

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Summary—*N,N*-Di-n-octylacetamide (DOAA) was prepared and shown to be an effective extractant for a number of metal ions from aqueous hydrochloric acid solution. Distribution ratios of 35 metal ions were measured for 1*M* DOAA in chloroform and hydrochloric acid solutions ranging from 0.10 to 9.0*M*. Extraction of uranium(VI) from solutions of hydrochloric acid and of nitric acid was compared. The effects of different diluents and varying concentrations of DOAA were studied in an attempt to elucidate the extraction mechanisms involved.

The extraction of some metal ions from nitrate and perchlorate media with liquid alkylacetamides has been studied by various investigators.[1–3] The thermal stability of amides was established to be comparable to that of tri-n-butyl phosphate (TBP).[4] Fritz and Orf[3] have shown that dihexylacetamide extracts uranium(VI) and thorium(IV) selectively from nitrate solutions. They also showed that although the extraction behaviour of dibutylacetamide and dihexylacetamide is similar, the solubility of the extractants in the aqueous phase decreases with increasing alkyl chain-length.

One aim of the present investigation was to decrease further the solubility of the extractants in the aqueous phase by the preparation of *N,N*-dioctylacetamide. A second aim was to study the behaviour of the new extractant with respect to metal species from media other than nitrate solutions, namely, hydrochloric acid of various concentrations. Distribution ratios were determined for metal ions in the system 1*M* *N,N*-dioctylacetamide (DOAA) in chloroform and hydrochloric acid of various concentrations. Distribution ratios for the uranyl species were determined with increasing amounts of both hydrochloric acid and nitric acid and the two systems compared.

EXPERIMENTAL

Reagents

Whenever possible, metal stock solutions were prepared by dissolution of reagent grade metal chlorides or oxides in hydrochloric acid.

N,N-Dioctylacetamide was prepared by reacting equal molar concentrations of acetic anhydride and di-n-octylamine overnight in the presence of diethyl ether. The reaction mixture was then treated with several portions of sodium bicarbonate solution to neutralize the acetic acid formed, followed by washing with 3*M* hydrochloric acid for the removal of unreacted amine. The organic phase was washed with water, then emulsified water was removed by addition of anhydrous sodium sulphate and after decantation the ether was evaporated. *N,N*-Dioctylacetamide was obtained as a clear, slightly yellowish liquid which, as shown by gas chromatography, was free from amine impurities.

Analytical techniques

Uranium,[5] platinum,[6] palladium,[6] rhodium,[7] antimony,[8] gold,[9] zirconium[10] and titanium[8] were determined spectrophotometrically after complex formation with the appropriate chromogenic agents. Molybdenum, thallium, tin, tellurium, selenium, iridium and ruthenium were determined by direct spectrophotometric measurement of their chloride complexes.[11] Antimony(III) was determined spectrographically by excitation in an induction-coupled plasma torch. Gallium, praseodymium, thorium and indium were determined by EDTA-titration and arsenic by iodometric titration. All other metals were determined by atomic-absorption spectrophotometry.

Determination of distribution coefficients

Aliquots (10 ml) of solutions containing 1–10 mg of the respective metal species and various concentrations of hydrochloric acid were shaken for 60 sec with 2 ml of a 1*M* solution of DOAA in chloroform. After phase separation the aqueous solutions were analysed for residual metal species present and the distribution ratios calculated according to:

$$D = \frac{\text{concentration of metal in the organic phase}}{\text{volume of the organic phase}} \times \frac{\text{volume of the aqueous phase}}{\text{concentration of metal in the aqueous phase}}.$$

The time needed for equilibrium to be reached during extraction was determined by shaking portions of 5*M* hydrochloric acid, each containing 1 mg of platinum, with 1*M* DOAA in chloroform (aqueous/organic phase-ratio 5) for various lengths of time. Maximum extraction of 86% of platinum was obtained after shaking for 30–60 sec. Thereafter a very slight decrease in the extraction rate was observed over a period of 10 min.

In an attempt to ensure reproducible species and oxidation states of the noble metals, solutions were used that had previously been evaporated to incipient dryness in the presence of sodium chlorate and hydrochloric acid.

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Table 1. Distribution ratios of metal ions for the system aqueous HCl–1*M* DOAA in chloroform

Species	Acid concentration, *M* 0.1	1.0	3.0	5.0	7.0	9.0
Mg(II)	—*	—	—	—	—	—
Al(III)	—	—	—	—	—	—
Ca(II)	0.1	0.4	0.9	1.1	1.5	2.1
Ti(II)	—	—	—	—	—	—
Cr(III)	—	—	—	—	—	—
Mn(II)	—	—	—	—	—	—
Fe(III)	—	0.04	6.7	495.0	∞	∞
Co(II)	—	0.2	0.3	0.3	0.5	1.3
Ni(II)	—	—	—	—	—	—
Cu(II)	0.04	0.2	0.2	0.6	2.0	2.1
Zn(II)	0.4	3.3	8.2	8.2	8.2	8.2
Ga(III)	0.3	0.3	12.2	187.3	∞	∞
As(III)	—	—	—	0.3	3.3	28.8
Se(IV)	3.3	2.5	1.2	0.02	1.4	2.3
Te(IV)	0.05	0.1	1.0	40.5	245.0	495.0
Zr(IV)	—	—	0.2	1.6	5.4	11.0
Mo(VI)	—	0.3	0.4	4.5	8.3	9.3
Ru(III)	5.0	0.9	0.3	1.0	1.0	0.3
Rh(III)	2.7	0.4	—	—	—	—
Pd(II)	14.3	0.3	—	0.7	2.3	0.7
Cd(II)	2.7	8.9	8.9	8.9	8.9	5.9
In(III)	—	0.3	1.0	1.6	2.6	15.8
Sn(IV)	—	—	0.3	22.0	146.5	245.0
Sb(III)	N.D.†	37.4	45.0	35.3	23.4	20.1
Sb(V)	ppt.	ppt.	5.0	13.7	39.6	105.0
Pr(III)	—	—	—	—	—	—
Ir(IV)	495.0	5.4	5.0	495.0	721.3	422.4
Pt(IV)	25.5	2.5	1.5	25.5	66.4	35.7
Au(III)	114.0	699.2	975.4	752.6	515.8	235.4
Hg(II)	92.7	67.8	57.5	65.2	88.1	88.1
Tl(III)	289.0	233.0	203.0	195.0	114.0	87.6
Pb(II)	—	—	—	—	—	—
Bi(III)	ppt.	0.2	0.2	0.2	0.2	0.2
Th(IV)	—	—	—	—	—	—
U(VI)	—	0.6	0.9	3.2	23.6	788.7

* — = Negligible extraction.
† N.D. not determined.

RESULTS

Extraction of metal ions

The *N,N*-dibutyl- and dihexylamides used by Fritz and Orf[3] for solvent extraction were excessively soluble in higher concentrations of nitric or hydrochloric acid, whereas the *N,N*-di-n-octylacetamide used in the present study is sufficiently insoluble and stable to be used effectively in concentrated hydrochloric acid and in nitric acid up to 10*M*.

A large number of metal ions were extracted from various concentrations of hydrochloric acid with 1*M* solutions of *N,N*-di-n-octylacetamide in chloroform. The results are tabulated in Table 1, and distribution ratios for selected metal ions are plotted in Figs. 1–3. Negligible extraction was obtained for several common metal ions such as chromium(III), manganese(II), nickel(II) and aluminium(III). Increasing extraction with increasing acid concentration was observed for those metal ions capable of forming solvated anionic chloride species, such as iron(III), uranium(VI) and to a lesser extent, cobalt(II) and copper(II). Gold(III) is extremely well extracted by DOAA over the entire concentration range tested. The platinum-group metal ions (Fig. 3) are extracted from 0.1*M* hydrochloric acid; the curves pass through a minimum at around 2*M* hydrochloric acid and attain a maximum at around 6–7*M* hydrochloric acid. The reason for this behaviour is not entirely clear, but it appears that different mechanisms of solvent extraction may be operative at the lower and at the higher acid concentrations.

That the choice of diluent has a pronounced effect on the extraction efficiency of the platinum metals is shown in Fig. 4, benzene being used instead of chloroform. With benzene, extraction of all the platinum metals increased at low acid concentrations and the extraction minima and maxima obtained when chloroform was used as the diluent were less pronounced.

From the distribution ratios shown in Table 1 it is clear that many useful separations are possible, particularly if it is borne in mind that extraction efficiency can be further improved by increasing the concentration of the amide extractant. For example, gold(III) can be separated from all other metal ions

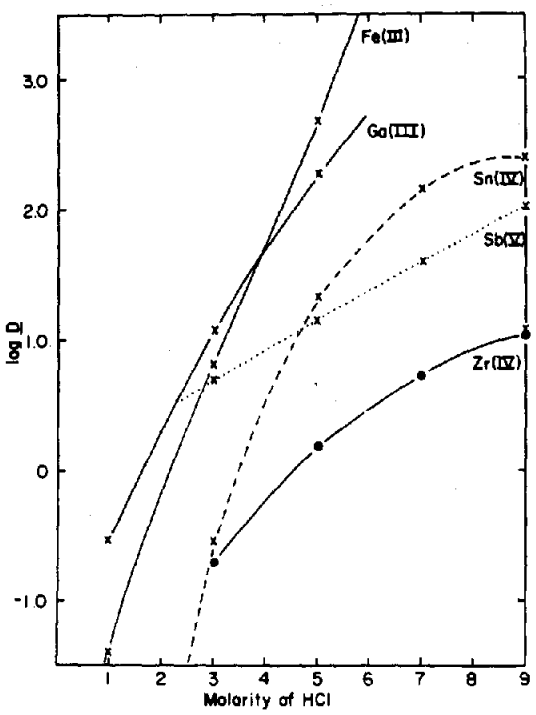

Fig. 1. Distribution ratios. System: HCl–1*M* DOAA in chloroform.

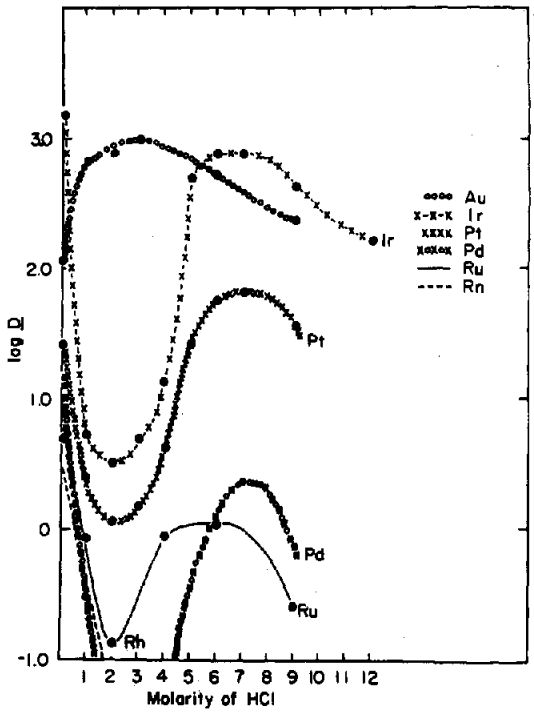

Fig. 3. Distribution ratios of noble metals. System: HCl–1*M* DOAA in chloroform.

tested except mercury(II) and thallium(III). Uranium(VI) can be separated from thorium(IV) and ruthenium(III). The noble metals as a group could possibly be separated. with the exception of mercury(II). thallium(III). selenium(IV) and cadmium(II). from all other metal ions studied at low acid concentrations.

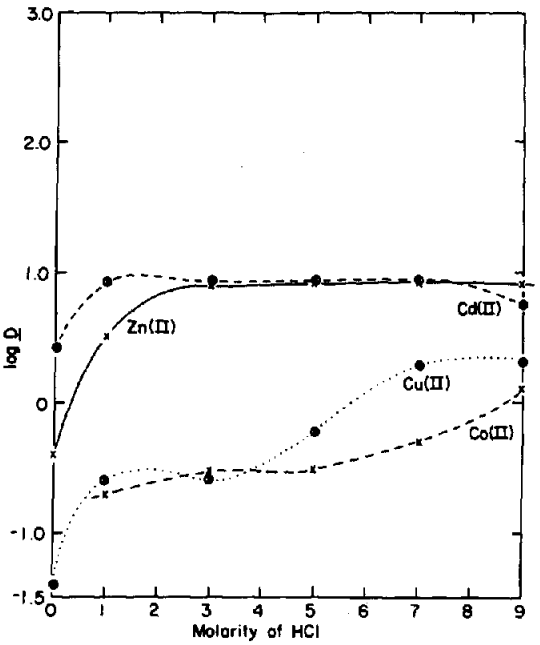

Fig. 2. Distribution ratios. System: HCl–1*M* DOAA in chloroform.

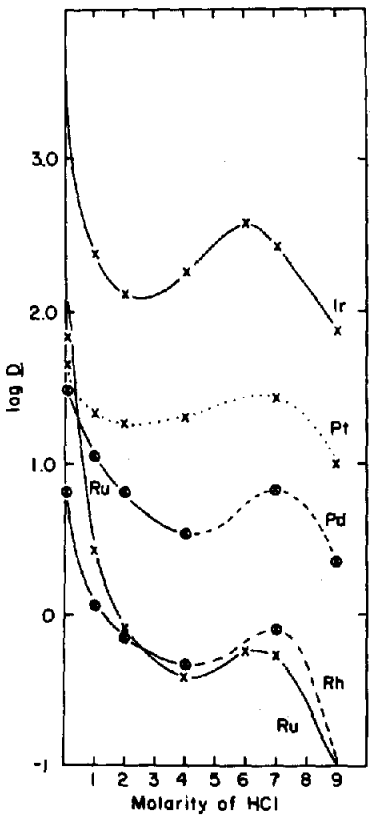

Fig. 4. Distribution ratios of noble metals. System: HCl–1*M* DOAA in benzene.

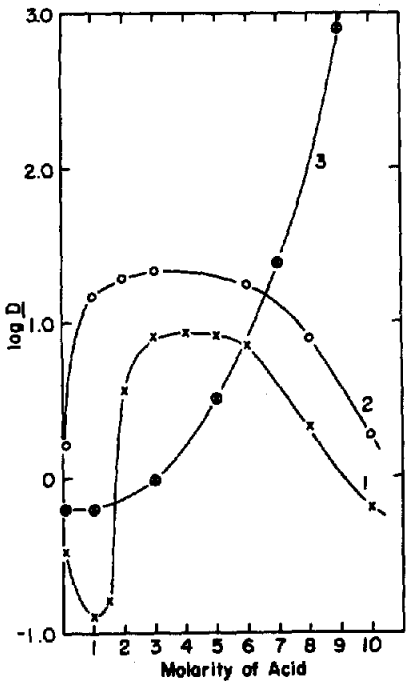

Fig. 5. Distribution ratios of uranium(VI). Systems: (1) HNO_3–1*M* DOAA in chloroform; (2) HNO_3–1*M* DOAA in benzene; (3) HCl–1*M* DOAA in chloroform.

Extraction of uranium

Fritz and Orf[3] have demonstrated the selective extraction of uranium(VI) with dihexylacetamide from nitrate solutions. The extraction of uranium(VI) with DOAA was therefore investigated in more detail. Distribution curves for uranium(VI) obtained by extraction with 1*M* DOAA solutions from both hydrochloric and nitric acids of various molarities are compared in Fig. 5. Bell-shaped curves with maxima at approximately 5*M* acid were obtained for the nitric acid system. In the hydrochloric acid system, distribution ratios increased with acid concentration up to the maximum concentration tested. Again, a distinct increase of distribution ratios was observed when benzene was used instead of chloroform as the diluent for the extractant (Fig. 5). This was even more pronounced when uranium was extracted from nitrate solutions at a pH value of 3 in the absence of excess of nitric acid, as shown in Table 2.

The extraction of uranium was found to be independent of pH in the range 1–4 at a constant nitrate concentration of 1*M*. However, a slightly negative pH value seemed to aid the extraction and the distribution ratio increased from 30 to 62 when the 1*M* nitrate solution was made 1*M* in nitric acid. The same was found to be true for the extraction of large amounts of uranyl nitrate (1.26*M*) into concentrated dioctylacetamide. (A small amount of diluent had to be added after extraction to prevent the organic phase from solidifying.) In the absence of nitric acid, 1.18 g of $UO_2(NO_3)_2$ was extracted per ml of DOAA, whereas in the presence of 1*M* nitric acid, 2.03 g $UO_2(NO_3)_2$ was extracted per ml of DOAA. Increasing the nitrate concentration in the absence of nitric acid and at constant amide concentration showed the expected increase in uranium extraction.

Mechanisms of extraction

Based on experimental evidence and theoretical considerations, an attempt was made to explain the mechanisms involved in the extraction of metal ions by DOAA. At fixed nitrate concentration and with no excess of nitric acid, a plot of log *D* for uranium(VI) *vs.* log amide concentration (in benzene) gave a linear plot with a slope of 1.8. Increasing the nitrate concentration in the absence of nitric acid and at constant amide concentration gave a straight-line plot of log *D vs.* log nitrate concentration with a slope of 1.9. These data suggest that the complex extracted has the formula $UO_2(Amide)_2(NO_3)_2$, which is in agreement with the findings of Fritz and Orf for another amide.[3] In this case it appears that the amide is serving as a ligand for the uranium.

Extraction of the platinum-group metals must involve a different mechanism, because replacement of chloride (as in $PtCl_6^{2-}$, for example) by another ligand would be slow, but the extraction rapidly attains a constant value. Figure 6 shows the spectra of the extracted species for iridium(IV) to be identical with that in aqueous solution. This suggests that no change in the inner-sphere complex has taken place.

Several of the platinum-group metals were extracted at varying amide concentrations and plots made of log *D vs.* log amide concentration at different acidities (Fig. 7). From the slopes of the plots obtained it appears that at low acid concentrations the extracted metal species contains approximately two amide molecules. Thus a reasonable mechanism seems to be the formation of an extractable ion-pair. For palladium(II) (present as $PdCl_4^{2-}$) as an example, the reaction can be represented as follows:

$$2\text{Amide(org)} + PdCl_4^{2-}\text{(aq)} + 2HCl\text{(aq)} \rightleftharpoons (HAmide)_2^{+}\,PdCl_4^{2-}\text{(org)} + 2Cl^-\text{(aq)}$$

As would be expected from the law of mass action, extractions at low acidities showed decreasing extraction with increasing concentrations of added chloride.

At the higher acidities indicated in Fig. 7 the slopes for the noble metals are greater. For example, palladium(II) has a slope of approximately 4.3 in 7*M* hy-

Table 2. Effect of organic diluents on the extraction of uranium(VI) (conditions: 10 mg of uranium, pH 3.0, aqueous:organic phase ratio 5.0, 1*M* $NaNO_3$ in aqueous phase)

Solvent	Extraction, %	Distribution coefficient, K_d
Chloroform	15	0.9
Petroleum ether	70	11.7
Toluene	75	15.0
Benzene	83	24.4

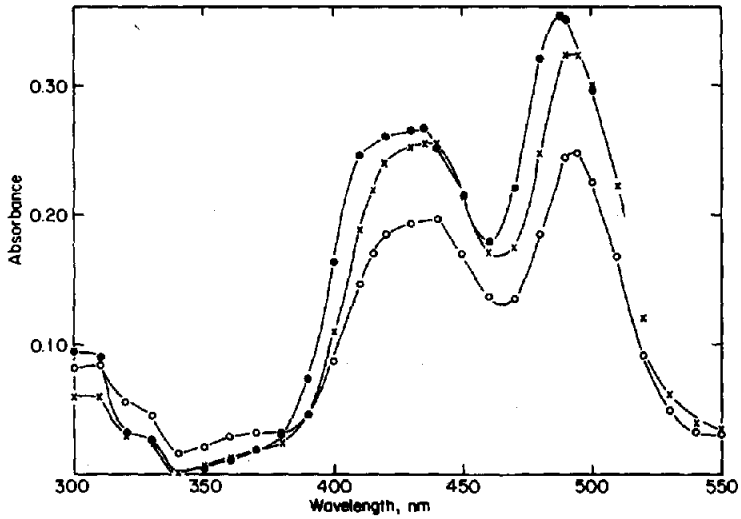

Fig. 6. Absorption spectra of iridium(IV): × extracted from 0.01*M* HCl; ○ extracted from 6*M* HCl; ● $IrCl_6^{2-}$ in aqueous solution.

drochloric acid. Diamond[12] suggested in his investigation on amine extraction systems that on decreasing the basicity of the amines, two or three molecules, instead of one, would be necessary to solvate the proton. Since an amide is a much weaker base than an amine, a similar mechanism can be visualized and would serve as an explanation for the higher slopes obtained in more acidic solutions.

CONCLUSION

Ishimori and Nakamura[13] have surveyed the behaviour of several organic solvents commonly used for the extraction of metal ions from hydrochloric and nitric acid solutions. Dioctylacetamide is a more powerful extractant than ethers and ketones and compares very favourably with tributyl phosphate (TBP). DOAA extracts the platinum-group metals more strongly than TBP and extracts several other metal ions to a slightly greater extent than TBP. DOAA lacks one major disadvantage of TBP, namely, that TBP can be partially hydrolysed to a substituted phosphoric acid, which is such a strong ligand that back-extraction of metal ions may be prevented.

For the reasons cited, it appears that amides in general, and dioctylacetamide in particular, are solvent extractants of major importance.

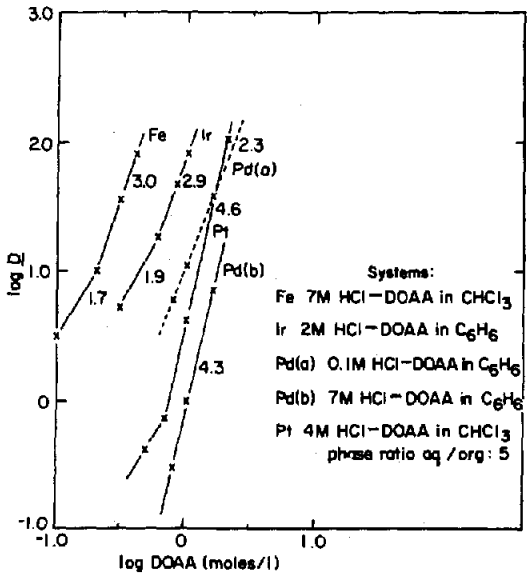

Fig. 7. Plots of log *D* *vs.* log DOAA concentration.

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DETERMINATION OF TRACES OF COPPER BY THE CATALYSED PEROXODISULPHATE–BROMIDE–ASCORBIC ACID LANDOLT REACTION

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Summary—The reaction between peroxodisulphate and bromide has been utilized for the catalytic determination of 0–1 ppm of copper in dissolved samples. The kinetics and mechanism of the uncatalysed and catalysed reaction have been studied, and the most important kinetic parameters determined. Under the experimental conditions described, the determination can be carried out in the presence of large numbers of other ions with an error less than 5%.

The application of catalysed Landolt reactions[1] in trace analysis offers several advantages over other methods: simplicity of operation (therefore no need for specially trained personnel), cheapness of instrumentation and the well-known features of kinetic methods,[2–4] which lead to high selectivity and sensitivity. Following earlier investigations[5,6] on catalytic Landolt reactions, we examined the peroxodisulphate–bromide–ascorbic acid Landolt system and applied it to the determination of copper in the 0–1 ppm concentration range.

EXPERIMENTAL

Reagents

Analytical-grade reagents were used.

The dimethyl-*p*-phenylenediamine indicator was obtained in vacuum-sealed phials. Once a phial was opened, decomposition took place rapidly but could be slowed down by storing the reagent at 0° in a screw-top glass container. Every fourth week a new phial was opened.

Procedure

All the reagents were brought to the same temperature (in a water-bath) before measurements were made. The experiments were done in test-tubes placed in the water-bath. The reagents were mixed manually with a flat-bottomed glass rod. All solutions were dispensed by pipette. Reaction vessels were dried before use.

RESULTS AND DISCUSSION

Stoichiometry, kinetics and mechanism of the reactions

Although the kinetics of reactions involving peroxodisulphates have been thoroughly studied in the past, no direct investigation of the peroxodisulphate–bromide reaction has been reported. An unpublished study reported in a review[7] gave rather inconclusive results, which are in disagreement both with our own studies and with the findings on the analogous peroxodisulphate–iodide reaction, which has been studied extensively in the past 80 years.[8–15] The catalytic action of copper on the peroxodisulphate–bromide reaction has also not been previously studied, but there are ample data in the literature of the role of copper as a catalyst in the oxidation of various other substances by peroxodisulphate.[13,16,17] The literature on silver-catalysed oxidations with peroxodisulphate[13–31] was also useful to us when formulating our views on the matter. We undertook a detailed kinetic study of both the uncatalysed and catalysed reactions, the details of which are published in a thesis.[32] Our findings can be summarized as follows.

The stoichiometry of both the uncatalysed and catalysed peroxodisulphate–bromide–ascorbic acid reaction can be described by the equation:

$$S_2O_8^{2-} + C_6H_8O_6 \rightarrow 2SO_4^{2-} + 2H^+ + C_6H_6O_6 \quad (1)$$

It should be emphasized that at the pH used in this study, this reaction would not proceed with measurable speed, in the absence of bromide. Once the ascorbic acid has been completely oxidized, bromine is formed in the mixture:

$$S_2O_8^{2-} + 2Br^- \rightarrow 2SO_4^{2-} + Br_2 \quad (2)$$

and this can be used to indicate the end of the period during which the concentration of peroxodisulphate falls to a predetermined value.

The mechanism of the uncatalysed reaction can be described in terms of the initial slow step:

$$S_2O_8^{2-} + Br^- \xrightarrow{k_{un}} Br + SO_4^{2-} + SO_4^- \quad (3)$$

followed by the fast steps

$$SO_4^- + Br^- \rightarrow Br + SO_4^{2-} \quad (4)$$

$$2Br \rightarrow Br_2 \quad (5)$$

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and by the Landolt-step in which ascorbic acid reduces bromine back to bromide:

$$Br_2 + C_6H_8O_6 \rightarrow 2Br^- + 2H^+ + C_6H_6O_6 \quad (6)$$

The sum of reactions (3)–(6) gives the overall stoichiometry expressed in (1).

It should be noted that this reaction scheme is a simplified one. For example, no account is taken of the well-known fact that the rates of these reactions are dependent on pH; however, as we did all the experiments in solutions buffered at a constant pH which was found most suitable for the determination of copper, this effect could be left out of consideration. The existence of sulphate radicals, involved in steps (3) and (4), has been proved experimentally beyond doubt,[27–31] and the formation of bromine atoms (Br) needs no further comment.

For the mechanism of the copper-catalysed reaction we could postulate various self-consistent schemes which would all fit the experimental results. The literature itself is divided in explaining the role of copper in such catalytic reactions. For us the most plausible mechanism involves the following three slow reaction steps

$$S_2O_8^{2-} + Cu^{2+} \xrightarrow{k_1} CuS_2O_8 \quad (7)$$

$$CuS_2O_8 \underset{}{\overset{k_2}{\rightarrow}} Cu^{2+} + S_2O_8^{2-} \quad (8)$$

$$CuS_2O_8 + Br^- \xrightarrow{k_3} Cu^{2+} + Br + SO_4^{2-} + SO_4^- \quad (9)$$

and these are followed by the fast steps (4), (5) and (6). The sum of (7)–(9) and (4)–(6) again gives the overall stoichometry expressed in (1).

The overall reaction rate in a reacting system which contains peroxodisulphate, bromide, ascorbic acid and copper is the sum of the individual rates of the uncatalysed and catalysed processes. The rate can be expressed as the rate of disappearance of peroxodisulphate:

$$-\frac{d[S_2O_8^{2-}]}{dt} = \left(-\frac{d[S_2O_8^{2-}]}{dt}\right)_{un} + \left(-\frac{d[S_2O_8^{2-}]}{dt}\right)_{cat} \quad (10)$$

The rate of the uncatalysed reaction, *cf.* equation (3), can be expressed as

$$\left(-\frac{d[S_2O_8^{2-}]}{dt}\right)_{un} = k_{un}[S_2O_8^{2-}][Br^-] \quad (11)$$

while the rate of the catalysed reaction, equation (9), is

$$-\left(\frac{d[S_2O_8^{2-}]}{dt}\right)_{cat} = k_3[CuS_2O_8][Br^-]. \quad (12)$$

The concentration of the species CuS_2O_8 is unknown and unmeasurable. It is however plausible that reaction (8) is very slow, meaning that a steady-state condition exists; that is, the concentration of CuS_2O_8 is both constant and low. This condition can be expressed by the equation:

$$\frac{d[CuS_2O_8]}{dt} = 0 = k_1[S_2O_8^{2-}][Cu^{2+}] - k_2[S_2O_8^{2-}] - k_3[CuS_2O_8][Br^-]. \quad (13)$$

In other words, the CuS_2O_8 species behaves as a van't Hoff complex.[33] Furthermore, we must keep in mind that the concentration of bromide ions is constant until the end of the measured incubation period and equals the analytical concentration of bromide:

$$[Br^-] = c_{Br^-} \quad (14)$$

Finally, for the analytical concentration of copper(II) ions ($c_{Cu^{2+}}$) the following mass-balance equation is valid:

$$c_{Cu^{2+}} = [Cu^{2+}] + [CuS_2O_8] \quad (15)$$

Equations (10)–(15) can be combined to give

$$\frac{d[S_2O_8^{2-}]}{dt} = k_{un}c_{Br^-}[S_2O_8^{2-}] + \frac{k_1k_3c_{Br^-}c_{Cu^{2+}}[S_2O_8^{2-}]}{k_1[S_2O_8^{2-}] + k_2 + k_3c_{Br^-}}. \quad (16)$$

This rate equation can be simplified by considering that, because of the steady-state condition,

$$k_3c_{Br^-} \gg k_1[S_2O_8^{2-}] + k_2. \quad (17)$$

By introduction of the notation

$$k_1 = k_{cat} \quad (18)$$

the rate equation is simplified to

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_{un}c_{Br^-}[S_2O_8^{2-}] + k_{cat}c_{Cu^{2+}}[S_2O_8^{2-}] \quad (19)$$

This rate equation can be simplified by considering that, because of the steady-state condition,

(*i*) if $t = 0$, then $[S_2O_8^{2-}] = [S_2O_8^{2-}]_0$

(*ii*) at the end of the incubation period (when the Landolt reaction time t_L is measured) if

$$t = t_L,$$

then

$$[S_2O_8^{2-}] = [S_2O_8^{2-}]_0 - [C_6H_8O_6]_0$$

[cf. the stoichiometry of reaction (1)]. The subscript 0 refers to the initial (and therefore known) concentrations. After separation of the variables, integration with these boundary conditions yields the expression

$$\ln\frac{[S_2O_8^{2-}]_0}{[S_2O_8^{2-}]_0 - [C_6H_8O_6]} = (k_{un}c_{Br^-} + k_{cat}c_{Cu^{2+}})t_L \quad (20)$$

Table 1. Determination of the k_{un} rate constant

$[S_2O_8^{2-}]_0$, M	$[C_6H_8O_6]_0$, M	c_{Br^-}, M	t_L^0, sec	k_{un}, l.mole^{-1}.sec^{-1}
6.21×10^{-2}	2.950×10^{-2}	0.474	120	1.13×10^{-2}
4.14×10^{-2}	1.967×10^{-2}	0.3158	176	0.98×10^{-2}
3.107×10^{-2}	1.475×10^{-2}	0.2369	231	1.18×10^{-2}
2.485×10^{-2}	1.180×10^{-2}	0.1895	285	1.19×10^{-2}
2.071×10^{-2}	9.83×10^{-3}	0.1579	354	1.15×10^{-2}
1.776×10^{-2}	8.43×10^{-3}	0.1353	410	1.16×10^{-2}
1.553×10^{-2}	7.38×10^{-3}	0.1184	465	1.16×10^{2}
1.553×10^{-2}	3.333×10^{-3}	0.1184	180	1.13×10^{-2}
$k_{un} = (1.14 \pm 0.06) \times 10^{-2}$ l.mole^{-1}.sec^{-1}		$n = 8$		mean: 1.14×10^{-2}
		$\tau_{(7,0.95)} = 2.36$		$s = 6.6 \times 10^{-4}$
				$\frac{\tau s}{\sqrt{n}} = 5.5 \times 10^{-4}$

The solutions contained a phosphate buffer of pH = 3.9 and were kept at 40°C.

This equation contains only measurable quantities, and it is therefore possible to determine the rate constants k_{un} and k_{cat} from the results of experiments carried out with various initial concentrations.

To prove that these considerations are consistent with experimental facts, we first carried out a series of measurements without copper present ($c_{Cu^{2+}} = 0$) and measured the blank reaction times t_L^0. Results were evaluated from (20) rearranged to

$$k_{un} = \frac{1}{t_L^0 c_{Br^-}} \ln \frac{[S_2O_8^{2-}]}{[S_2O_8^{2-}]_0 - [C_6H_8O_6]_0}. \quad (21)$$

Stock solutions of potassium peroxodisulphate, ammonium bromide and ascorbic acid were made up, and diluted to various degrees with an acetate buffer of pH 3.9. All the solutions also contained ammonium fluoride to make their composition similar to the reagent solution used for analysis (see later). Reaction times were measured at 40°, under the conditions described under the experimental section. The results summarized in Table 1 indicate that for a wide range of concentrations the k_{un} value is really constant, substantiating the mechanistic and kinetic considerations given above for the uncatalysed process. The value $k_{un} = 1.14 \times 10^{-2}$ l.mole^{-1}.sec^{-1} (standard deviation 6.6×10^{-4}) is accepted for the uncatalysed rate constant.

In a second series of measurements we used the same experimental circumstances as in the first, but all solutions contained a known concentration of copper(II) sulphate. In the first experiment this concentration ($2.623 \times 10^{-6} M$) corresponded to 0.5 ppm copper content in the test solution, that is, to the middle of the analytically useful concentration range. The t_L reaction times were measured, and the k_{cat} rate constants were calculated from the following equation, obtained by rearranging (20):

$$k_{cat} = \left\{ \frac{1}{t_L} \ln \frac{[S_2O_8^{2-}]_0}{[S_2O_8^{2-}]_0 - [C_6H_8O_6]_0} - k_{un} c_{Br^-} \right\} \times \frac{1}{c_{Cu^{2+}}} \quad (22)$$

Results are shown in Table 2. These again verify the mechanism and kinetics described for the catalysed process. The value 9.7×10^2 l.mole^{-1}.sec^{-1} (standard deviation 1.5×10^2) can be accepted for the catalysed rate constant. The particular shape of the calibration curve (see later) is also consistent with equation (20).

Our kinetic study involved the determination of the enthalpies and entropies of activation for the uncatalysed and catalysed reactions. According to the activated-complex theory of reaction rates, the rate con-

Table 2. Determination of the k_{cat} rate constant

$[S_2O_8^{2-}]_0$, M	$[C_6H_8O_6]_0$, M	c_{Br^-} M	$c_{Cu^{2+}}$, M	t_L, sec	k_{cat}, l.mole^{-1}.sec^{-1}
6.21×10^{-2}	2.950×10^{-2}	0.4737	2.623×10^{-6}	82	9.45×10^{2}
4.14×10^{-2}	1.967×10^{-2}	0.3158	1.749×10^{-6}	132	7.3×10^{2}
3.107×10^{-2}	1.475×10^{-2}	0.2369	1.312×10^{-6}	171	8.1×10^{2}
2.485×10^{-2}	1.180×10^{-2}	0.1895	1.049×10^{-6}	197	10.6×10^{2}
2.071×10^{-2}	9.83×10^{-3}	0.1579	0.874×10^{-6}	243	9.7×10^{2}
1.776×10^{-2}	8.43×10^{-3}	0.1353	0.749×10^{-6}	283	9.8×10^{2}
1.553×10^{-2}	7.3×10^{-3}	0.1184	0.656×10^{-6}	314	10.7×10^{2}
1.553×10^{-2}	3.333×10^{-3}	0.1184	2.623×10^{-6}	54	11.9×10^{2}
$k_{cat} = (9.7 \pm 1.2) \times 10^2$ l.mole^{-1}.sec^{-1}			$n = 8$		mean: 9.7×10^{2}
			$\tau_{(7,0.95)} = 2.36$		$s = 1.5 \times 10^{2}$
					$\frac{\tau s}{\sqrt{n}} = 1.2 \times 10^{2}$

Table 3. Determination of the entropy and enthalpy of activation of the uncatalysed reaction
$[S_2O_8^{2-}]_0 = 1.553 \times 10^{-2}M$
$c_{Br^-} = 0.1184M$
$[C_6H_8O_6]_0 = 3.333 \times 10^{-3}M$

Temperature, °C	$1/T, K^{-1}$	$t^0_{L,T}$, sec	$F(T)_{un}$	$k_{T,un}$, $l.mole^{-1}.sec^{-1}$
30	3.30×10^{-3}	394	−288.811	5.16×10^{-3}
35	3.25×10^{-3}	262	−285.570	7.83×10^{-3}
40	3.19×10^{-3}	174	−282.295	1.17×10^{-2}
45	3.14×10^{-3}	116	−279.084	1.74×10^{-2}

$\Delta H^*_{un} = (62.4 \pm 2.9) \times 10^3\ J^{-1}\ mole$
$\Delta S^*_{un} = -83.0 \pm 9.4\ J.mole^{-1}.deg^{-1}$

stant can be expressed in terms of the energy (ΔH^*) and enthalpy (ΔS^*) of activation in the following way:[34]

$$k = \frac{\mathbf{k}T}{h} \exp\left[-\frac{\Delta H^*}{RT}\right] \exp\left[\frac{\Delta S^*}{R}\right] \qquad (23)$$

where $\mathbf{k}$ is the Boltzmann constant (1.381×10^{-23} J deg^{-1}), h Planck's constant (6.626×10^{-34} J.sec), R the gas constant (8.314 J.mole^{-1}.deg^{-1}) and T is the absolute temperature. The expression can be applied to both the uncatalysed and the catalysed process. Combining expressions (21) and (23) we can define an $F(T)_{un}$ temperature function for the uncatalysed process, as follows:

$$F(T)_{un} = R \ln\left\{\frac{h}{t^0_{L,T} c_{Br^-} \mathbf{k}T} \ln \frac{[S_2O_8^{2-}]_0}{[S_2O_8^{2-}]_0 - [C_6H_8O_6]_0}\right\} = \Delta S^*_{un} - \frac{\Delta H^*_{un}}{T}. \qquad (24)$$

From the uncatalysed reaction times $t^0_{L,T}$ at various absolute temperatures T, the values of the temperature function can be calculated and plotted as a function of $1/T$. The points should fall on a straight line, with intercept equal to the entropy, and slope equal to the enthalpy of activation. The results shown in Table 3 conform with this expectation. The values of the entropy and enthalpy of activation and their standard deviations were obtained by linear regression analysis. Values of the $k_{T,un}$ rate constants for the appropriate temperatures were calculated from expression (23). The value for 313 K (1.17×10^{-2}) agrees well with the value obtained from Table 1 (1.14×10^{-2}); the slight difference is probably due to the difficulty of reproducing the low ascorbic acid concentrations accurately when making up the reagent solutions.

Combining equations (22) and (23) we can also define an $F(T)_{cat}$ temperature function for the catalysed reaction:

$$F(T)_{cat} = R \ln\left(\frac{h}{\mathbf{k}T c_{Cu^{2+}}}\left[\frac{1}{t_{L,T} c_{Br^-}} \times \ln\left\{\frac{[S_2O_8^{2-}]_0}{[S_2O_8^{2-}]_0 - [C_6H_8O_6]_0}\right\} - k_{T,un}\right]\right) = \Delta S^*_{cat} - \frac{\Delta H^*_{cat}}{T}. \qquad (25)$$

and evaluate it as before. As Table 4 demonstrates, there is again a straight line relationship so the entropy and enthalpy of activation for the catalysed reaction can be calculated. The enthalpy of activation of the catalysed process is higher than that of the uncatalysed reaction; however, this is compensated by the more negative entropy of activation. In the language of the collision theory of reaction rates, the catalytic action can be explained by the increase in the pre-exponential factor. The $k_{T,cat}$ rate constants in Table 4 were calculated from expression (23). The

Table 4. Determination of the entrapy and enthalpy of activation of the catalysed reaction
$[S_2O_8^{2-}]_0 = 1.553 \times 10^{-2}M$
$c_{Br^-} = 0.1184M$
$[C_6H_8O_6]_0 = 3.333 \times 10^{-3}M$
$c_{Cu^{2+}} = 3.147 \times 10^{-6}M$

Temperature, °C	$1/I, K^{-1}$	$t_{L,T}$, sec	$F(T)_{cat}$	$k_{T,cat}$, $l.mole^{-1}.sec^{-1}$
30	3.30×10^{-3}	149	−197.113	3.18×10^2
35	3.25×10^{-3}	90	−192.677	5.61×10^2
40	3.19×10^{-3}	54	−188.073	9.73×10^2
45	3.14×10^{-3}	33	−183.761	1.66×10^1

$\Delta H^*_{cat} = (85.9 \pm 3.9) \times 10^3\ J\ mole^{-1}$
$\Delta S^*_{cat} = 86.1 \pm 12.6\ J.mole^{-1}.deg^{-1}$

value for 313 K agrees reasonably with the figure obtained from Table 2.

When comparing the precision of the results for the uncatalysed and catalysed process, we notice that the values obtained for the catalysed reaction are less precise than those for the uncatalysed process. This is expected, as expressions (22) and (25) contain the k_{un} rate constant, which itself has to be determined experimentally. All the errors involved in its measurement appear again, in the constants of the catalysed reaction.

Results of experiments carried out at different temperatures indicate how important it is to keep the temperature constant when carrying out such measurements.

The analytical sensitivity of this method (*i.e.*, the slope of the calibration curve) was found to increase with increasing temperature. This would suggest that the temperature should be raised to 318 K or even higher to optimize the method. With increasing temperature, however, the standard deviation increases, so 313 K was chosen, by compromise between precision and sensitivity, as the recommended temperature. It was also found that the reaction times at this temperature are conveniently measurable and that the indicator reaction is very sharp under these circumstances. The concentrations of reagents (including masking agents) as well as the pH of the medium were chosen on the basis of a lengthy optimization process guided by kinetics, in which the analytical sensitivity and selectivity were the main factors considered. We found that good selectivity required a relatively high bromide concentration, while according to the kinetics [equation (19)] of the processes, a low bromide concentration would offer better sensitivity. Here again a compromise had to be reached.

Determination of copper

On the basis of preliminary experiments, in which we tried to optimize the experimental conditions, we recommend the following procedure for the determination of copper in solutions of 0–1 ppm concentration.

Prepare reagents IA and IIA (or IIB, if iron is absent from the sample), having the compositions given in Table 5. Keep these solutions in a thermostat, adjusted to 40.0 ± 0.5°. Dispense 5.00 ml of the sample solution (containing less than 5 μg of copper) into a clean dry test-tube, kept in a test-tube rack immersed in the thermostat. In other test-tubes place 5.00 ml of copper solutions of known concentrations (between 0.1 and 1 ppm), and prepare a blank test with 5.00 ml of distilled water in another test-tube. Equip each test-tube with a dry glass rod for stirring (glass rods with a flattened end are most suitable). Allow time for thermal equilibration, then dispense 5.00 ml of solution II into each test-tube and mix. Now add 5.00 ml of solution I to the contents of the first test-tube, starting a stop-watch as the first drops enter the tube. Mix the contents and stop the watch when, after an incubation period of 0.5–4 min, the solution turns deep red. Note the reaction time, and repeat the procedure with the standards and the blank. The colour develops to its full extent within a few seconds, then slowly fades because the bromine formed in the reaction oxidizes the dimethyl-*p*-phenylenediamine indicator to a colourless product, the solution remaining yellowish-brown. It is therefore very easy to measure the reaction time; the watch must be stopped when the colour is most intense. The results can be evaluated with a calibration graph, in the manner described below.

The standard deviation of the time measurements, according to our experience, is not higher than 2 sec. It is advisable to carry out replicate measurements and accept only those results for which the reproducibility is adequate.

For evaluation a calibration graph has to be constructed. To do this, first calculate the average of the blank reaction times (t_L^0), then calculate the averages of the reaction times obtained for each sample and standard (t_L). Calculate the t_L^0/t_L ratios and plot them *vs* copper concentration. As already indicated, a straight line relationship is expected, with an intercept of unity on the t_L^0/t_L axis.

Although, according to the law of propagation of errors, experimental errors are accumulated in calculating the t_L^0/t_L ratio, we still recommend this procedure for evaluation, because we have found that when a new pair of reagent solutions is made up, the individual reaction times (t_L^0 and t_L) may alter considerably (variations of 20% are not uncommon) but their ratios are reproducible within a few per cent. For precise work, however, it is advisable to prepare a calibration curve daily. In such cases the $1/t_L$ values can be plotted instead of the t_L^0/t_L values; the calibration curve is still a straight line, with intercept $1/t_L^0$.

Table 5. Composition of reagent solutions

Method A	
Solution IA	Solution IIA
$K_2S_2O_8$ 12.60 g	NH_4Br 34.8 g
NaOH 13.33 g	NaOH 13.33 g
NH_4F 20.00 g	Ascorbic acid 0.88 g
Conc. CH_3COOH 100 ml per litre	Dimethyl-*p*-phenylenediamine 0.04 g
	Conc. CH_3COOH 100 ml per litre
Method B	
Solution IB	Solution IIB
$K_2S_2O_8$ 12.60 g	NH_4Br 34.8 g
NaOH 13.33 g	NaOH 13.33 g
KH_2PO_4 20.00 g	Ascorbic acid 1.76 g
Conc. CH_3COOH 100 ml per litre	Dimethyl-*p*-phenylenediamine 0.04 g
	Conc. CH_3COOH 100 ml per litre

Table 6. Results obtained with methods A and B

$c_{Cu^{2+}}$, ppm	t_L, min		t_L^0/t_L	
	A	B	A	B
0	3.64	3.08	1.00	1.00
0.1	2.59	2.13	1.41	1.44
0.2	1.85	1.63	1.97	1.89
0.3	1.51	1.32	2.41	2.33
0.4	1.32	1.13	2.76	2.73
0.5	1.11	0.95	3.28	3.24
0.6	0.99	0.87	3.68	3.54
0.7	0.87	0.78	4.18	3.95
0.8	0.78	0.71	4.67	4.34
0.9	0.72	0.64	5.06	4.81
1.0	0.66	0.59	5.52	5.22

Table 7. Statistical analysis of the calibration lines (Table 6)

	Method A	Method B
Intercept, a	1.00_5	1.04_5
Slope, b	4.52	4.18
Correlation coefficient r	0.9996	0.9995
$s\left\{\frac{t_L^0}{t_L}/c_{Cu^{2+}}\right\}$	4.13×10^{-2}	4.45×10^{-2}
s_a	2.3×10^{-2}	2.5×10^{-2}
s_b	3.9×10^{-2}	4.2×10^{-2}
Lowest determinable concentration c_{min}, ppm	0.021	0.025

s = standard deviation

Results for copper

Results are shown in Table 6 and statistical information on the precision is given in Table 7. The lowest determinable concentration was calculated, according to Doerffel,[35] from the equation:

$$c_{min} = \frac{\tau(s_a + \bar{c}s_b)}{b + \tau s_b} \qquad (26)$$

where a and b are the intercept and slope respectively, τ is the value of Student's t (for $f = 11 - 2 = 9$ degrees of freedom and level of significance $P = 0.95$, $\tau = 2.26$).

As seen from the results, method A (with fluoride as masking agent) is marginally more sensitive and precise than method B, but there is little difference

Table 8. Effect of foreign ions on ratio of reaction times ($t_{masked}/t_{unmasked}$)

	Masking agent									
	NH_4F (method A)					KH_2PO_4 (method B)				
	Concentration of ion, ppm									
Ion	1000	100	10	1.0	0.1	1000	100	10	1.0	0.1
V(V)	*	1.07	1.02			†	1.06	1.04		
Fe(III)	2.33	1.03				17.50	3.39	1.64	1.07	1.03
Fe(II)	1.25	1.00				4.95	3.47	1.70	1.11	1.02
Mo(VI)	1.19	1.01				1.14	1.05			
Os(VIII)	†	1.14	1.10	1.03		†	1.13	1.11	1.05	
Ce(III)	1.13	1.05				0.82	0.99			
Co(II)	1.05					1.13	1.04			
U(VI)	1.04					1.04				
Ti(III)	1.04					0.91	0.99			
Y(III)	1.03					0.96				
Mn(II)	1.02					1.10	1.04			
Ca(II)	1.02					1.07	1.04			
Ag(I)	1.02					1.01				
Sr(II)	1.01					1.03				
Ba(II)	1.01					1.03				
Hg(I)	1.01					1.07	1.05			
Hg(II)	1.03					1.03				
Mg(II)	1.01					1.01				
La(III)	1.01					0.72	0.96			
Zn(II)	1.00					1.03				
Ni(II)	1.00					1.04				
Ce(IV)	0.99					0.78	1.02			
Zr(IV)	0.98					0.96				
Pb(II)	0.98					1.04				
Al(III)	0.98					0.94	1.03			
Cd(II)	0.98					1.03				
Au(III)	†	0.96				†	0.84	1.02		
Re(VII)	0.95					1.03				
Cr(III)	0.95					0.97				
Sb(III)	0.88	0.98				0.81	0.90	1.00		
Se(VI)	0.78	1.04				0.82	1.03			
W(VI)	0.54	0.68	0.98			0.58	0.61	1.03		
Sn(II)	†	0.97				†	0.91	1.05		
Sn(IV)	†	0.85	1.00			†	0.86	1.00		

* Immediate Landolt effect.
† No visible Landolt effect.

between their performances. Keeping the fluoride solution in a glass vessel for longer times inevitably results in the glass surface being attacked, and this problem does not exist with the phosphate used in method B. On the other hand, phosphates are good media for micro-organisms, and the bacterial growth in such solutions can sometimes be observed.

It must also be said that the dimethyl-*p*-phenylenediamine indicator can be replaced by a mixture of Methyl Red and Methylene Blue (the well-known screened indicator used in acid–base titrimetry), of which 1 drop is sufficient for the 15 ml of mixture. In this case decolorization of the indicator marks the end of the Landolt reaction. As the decolorization is somewhat slower than the colour change of the dimethyl-*p*-phenylenediamine, the subjective error of the time measurement is higher, yielding a somewhat higher standard deviation (3 sec). Better results can be obtained if the concentrations of some of the reagents are increased (42.0 g of $K_2S_2O_8$, 180.5 g of NH_4Br and 1.76 g of ascorbic acid instead of the values given in Table 5). With such solutions reaction times are lower ($t_{\frac{1}{2}}^0$ = 1.5 min), but the decolorization of the indicator is easier to see. The slope of the calibration graph is somewhat lower in this case (about 2.8 ppm^{-1}).

The selectivity of the method was tested by measuring the Landolt reaction time, with 0.5 ppm copper present, in the presence of 34 different ions at 0.1, 1, 10, 100 and 1000 ppm concentrations. The reaction times were compared with the times obtained in the absence of the interferent. The experiments were first done with complexing agents absent, then repeated with them present to suppress interferences (fluoride, phosphate, citrate, tartrate, cyanide and EDTA were used). As the result of these experiments we came to the conclusion that fluoride and (in the absence of iron) phosphate are the best masking agents. Results obtained with these ions present are summarized in Table 8. The figures shown in the table are the ratios of reaction times obtained in the presence and absence of the interferent. The more a given value in the table differs from 1.00, the greater the interference. Figures between 0.95 and 1.05 represent errors of less than 5%. All the blank spaces in the table represent values between 1.00 and the last value shown for the particular ion, *i.e.*, they mean that there is no interference at all. As the results indicate, only osmium interferes at the 10-ppm level, vanadium, tungsten and tin(IV) at the 100-ppm level, and iron, molybdenum, antimony and selenium at the 1000-ppm level would cause marked errors. The selectivity towards iron is somewhat reduced if phosphate is used instead of fluoride, and also gold shows interference at the 100-ppm level. The effect of all the other ions tested is negligible.

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SHORT COMMUNICATIONS

TITRATION OF SOME THIAZINE DYES WITH $TiCl_3$ AT ROOM TEMPERATURE

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Summary—Methylene Blue and some other thiazine dyes are titrated at room temperature visually and potentiometrically in presence of 0.005–0.1 *N* oxalic acid. The effect of oxalic acid on the conditional potentials of the Ti(IV)/Ti(III) couple is presented.

Methylene Blue has been determined by titration with titanous chloride[1] in hydrochloric acid medium at 35° and in various acid media at higher concentrations.[2] From these earlier observations it is clear that the reaction between thiazine dyes and titanium(III) is slow at room temperature. Recently Murty *et al.*[3] observed that in titration of quinone with titanous chloride, oxalic acid catalyses the slow reaction between thiazine dyes and titanium(III). The observation has been utilized for the detection of oxalic acid.[4] It follows that oxalic acid can be used as catalyst in titration of thiazine dyes with titanium(III) at room temperature. To illustrate this effect, the conditional potentials of the Ti(IV)/Ti(III) couple have been determined in various acid media in the presence and absence of oxalic acid.

EXPERIMENTAL

Reagents

Titanium(III) chloride solution (0.02*M*) prepared from commercial 15% solution.

Aqueous solutions (0.0025*M*) of Methylene Blue, New Methylene Blue, Toluidine Blue, thionine, Methylene Green and 0.001*M* solutions of Azure C and Azure B prepared in demineralized water and standardized by titration with titanous chloride at elevated temperature.

Oxalic acid solution, 0.5*M*.

Procedure

An aliquot of dye solution and the volume of oxalic acid required to give the desired concentration (Table 1) are taken in a titration vessel fitted with a three-holed rubber stopper, one hole for the tip of the microburette and the other two as inlet and outlet for CO_2. Then CO_2 is passed through the solution for about 10 min and the contents are titrated with titanous chloride solution to the disappearance of the dye colour (in the case of Methylene Green, the colour transition is from green to pink). Results and the limits of oxalic acid concentrations are given in Table 1. The mineral acid concentrations may be varied from 0.1 to 4*N*.

The dyes can also be titrated potentiometrically, with an SCE reference electrode and a bright platinum rod as indicator electrode, and a saturated potassium chloride salt bridge. The potential becomes stable immediately, after each addition of titrant.

Table 1. Conditions and results of the titration of thiazine dyes with $TiCl_3$

Dye	Concentration of oxalic acid, *N*	Range determined, *mg*	Average error, %	Potential jump, *mV*/0.04 *ml*
Methylene Blue	0.01–0.5	20.0–2.0	0.1 (0.2)	240–250
Thionine	0.005–0.1	20.0–2.0	0.2 (0.2)	240–250
New Methylene Blue	0.005–0.1	20.0–2.0	0.1 (0.2)	110–120
Toluidine Blue	0.005–0.1	20.0–2.0	0.2 (0.3)	85–90
Methylene Green	0.005–0.01	20.0–2.0	0.3 (0.4)	30–40
Azure B	0.005–0.5	10.0–2.0	0.2 (0.3)	40–50
Azure C	0.005–0.5	10.0–2.0	0.3 (0.3)	160–170

* Values in parentheses correspond to visual method.

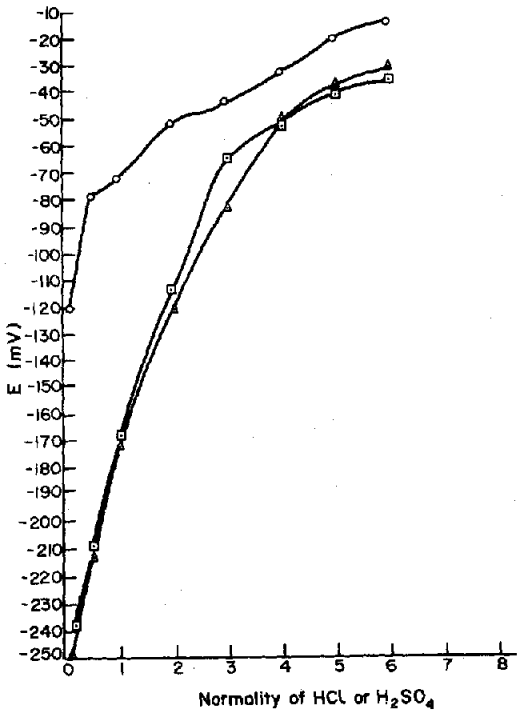

Fig. 1. Conditional redox potentials of Ti(IV)/Ti(III) at various concentrations of HCl or H_2SO_4 in the absence and presence of 0.05*N* $H_2C_2O_4$. O——O HCl; Δ——Δ HCl + $H_2C_2O_4$; □——□ H_2SO_4 + $H_2C_2O_4$.

DISCUSSION

In the absence of oxalic acid, the titration at room temperature gives non-reproducible results with positive errors, and in potentiometric titration the potential takes 3 min to become stable near the end-point. Figures 1 and 2 show the effect of oxalic acid and total acidity on the conditional potential. It is clear that oxalic acid (up to a certain concentration) lowers the potentials.

The mechanism involved is presumably that oxalic acid forms a complex with titanium(IV) and this results in a lowering of the potential of the Ti(IV)/Ti(III) couple. The drop in potential is not so pronounced at high as at low mineral acid concentration, which may be attributed to the decreasing stability

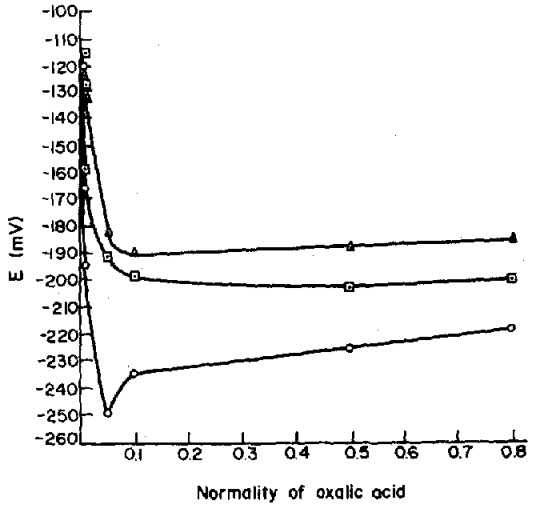

Fig. 2. Conditional redox potentials of Ti(IV)/Ti(III) at various $H_2C_2O_4$ concentrations in HCl or H_2SO_4. O——O 0.1*N* HCl; Δ——Δ 1.0*N* HCl; □——□ 1.0*N* H_2SO_4.

of the titanium(IV)-oxalic acid complex with increase in acid concentration. Stable potentials are not obtained for the Ti(IV)/Ti(III) couple in sulphuric acid. It is also seen from Fig. 2 that at a fixed mineral acid concentration the effect of oxalic acid is two-fold—there is first a rapid decrease in potential as the oxalic acid concentration increases, but this is counterbalanced by the increased hydrogen ion concentration when the oxalic acid concentration rises above a certain level.

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BIOASSAY OF NYSTATIN: MEASUREMENT OF Mg^{2+} EFFLUX BY ATOMIC-ABSORPTION SPECTROSCOPY

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Summary—A rapid bioassay for the polyene antibiotic nystatin, based on the leakage of Mg^{2+} from sensitive cells of *Saccharomyces cerevisiae*, is described. The assay employs atomic-absorption spectrophotometry to measure the Mg^{2+} leaked. It compares favourably with the classical method of diffusion on an agar-plate, in terms of speed, reproducibility and convenience.

The principal effects of polyene antibiotic action on susceptible cells have been recognized since the early 1960s as the leakage of vital cytoplasmic constituents. These are K^+, NH_4^+, amino-acids, Mg^{2+} and nucleotides.[1–6] Conway[6] found release of K^+ and NH_4^+ to be rapid, in agreement with the other literature, but that of Mg^{2+} to be slow. In this laboratory, studies on the kinetics of efflux of Mg^{2+} from yeast cells under the influence of nystatin gave an indication that a bioassay could be based upon the efflux of this ion. Bioassays based on the release of one or more cellular constituents have been described and are recommended by the reporting authors as alternatives to the time-consuming and somewhat less accurate microbiological assays.[7,8] Calorimetric assays[9,10] based on observation of the overall metabolism of the cells are at present not suitable for routine laboratory use because of the low throughput and the costly instrumentation. Evans *et al.*[11] and Smithler *et al.*[12] reported a bioassay that measured the amount of material leaked from sensitive cells, that would give a positive reaction with ninhydrin. Since these assays measure more than one material they are rather inaccurate and not very reproducible. Assays[13,14] based on the leakage of K^+ are not suitable for routine use in laboratories where potassium-containing buffers are in common use. The Rb^+ released from responsive cells has been shown to be conveniently measured with an ion-selective electrode[15] or atomic-absorption spectrophotometry.[16] However, these systems suffer the disadvantage that Rb^+ has to be introduced into the cells since it is not a natural constituent of yeast cells. The consequences of this incorporation into yeast cells are not well understood. In addition, incorporation of Rb^+ into the growth medium adds an unnecessary expense to a potential routine procedure. The ion-selective electrode system may be of advantage when new laboratories are being designed, where automated flow systems could be installed. However, for established laboratories the need may be for an assay system for which the apparatus is already available to the analyst.

Hence an assay based atomic-absorption measurement of the efflux of Mg^{2+} (a natural constituent of the yeast cell) is reported here.

EXPERIMENTAL

Materials

Saccharomyces cerevisiae (NCYC 239, Brewing Industry Research Foundation, Nutfield, Surrey) was used as the test organism. The culture was maintained, prepared and stored in liquid nitrogen as previously described.[17] For comparison and to investigate the effects of freezing and thawing of yeast inocula on the release of Mg^{2+}, fresh cultures were also prepared and studied. Fresh inocula were prepared in the same manner as the frozen inocula, except that the incubation period was increased to 20 hr during growth (in both cases the cells produced belonged to the late exponential or early stationary phase of growth).

The nystatin used throughout this study was kindly donated by Messrs. E. R. Squibb and Sons Ltd., Merseyside (Batch No. D2405). A weight containing 4×10^5 units of activity (IU) was dissolved in 100 ml of dimethylformamide (DMF). Dilutions to 50 times the levels of nystatin required were made in 0.05*M* citrate buffer (pH 4.4), DMF being added to yield a final concentration of 10%. In use these solutions were further diluted (see below) and produced a DMF concentration of 0.2%.

Magnesium leakage

The absorbances of recovered suspensions of *Saccharomyces cerevisiae* (cells stored in a cryostat, thawed for 3 min at 40° and suspended in 0.05*M* citrate buffer) in 1-cm cells at 570 nm were adjusted to 1.0. This corresponded to a cell density of 1.3×10^7 cells/ml.

Appropriate nystatin solutions were prepared and an accurate addition of 0.1 ml of each was made to 4.9-ml volumes of the cell suspension in centrifuge tubes. A cell blank and a reagent blank (0.2% DMF) were included in each set of determinations. The loaded tubes were incubated in a shaking water-bath for 30 min at 37°. These conditions were determined from preliminary studies. After incubation the tubes were centrifuged at 3000 rpm for 3 min, the supernatant phases were removed and placed in clean universal tubes and their Mg^{2+} content was determined by atomic-absorption spectrophotometry (Perkin-Elmer model 103) with an air–acetylene flame. The 285.2-nm line of a conventional Mg^{2+}/Ca^{2+} hollow-cathode lamp was used. The instrument was calibrated according to the manufacturer's instructions with standard

Table 1. The efflux of Mg^{2+} from freshly prepared inocula of *S. cerevisiae* that have been exposed to various concentrations of nystatin

Nystatin, *IU/ml*	Mg^{2+} in supernatant liquid, *μg/ml*						
	Day 1	Day 2	Day 3	Day 4	Day 5	Mean	Std. devn.
10	0.99	1.00	1.02	0.97	1.00	1.00	0.038
8	0.82	0.79	0.83	0.86	0.80	0.82	0.055
6	0.70	0.68	0.67	0.65	0.69	0.68	0.039
4	0.53	0.52	0.47	0.49	0.54	0.52	0.063
2	0.38	0.35	0.34	0.36	0.38	0.36	0.036
DMF control	0.32	0.29	0.30	0.31	0.34	0.31	0.039
Cell blank	0.27	0.30	0.32	0.29	0.31	0.30	0.037

Table 2. The efflux of Mg^{2+} from inocula (stored in liquid nitrogen) of *S. cerevisiae* that have been exposed to various concentrations of nystatin

Nystatin, *IU/ml*	Mg^{2+} in supernatant liquid, *μg/ml*						
	Day 1	Day 2	Day 3	Day 4	Day 5	Mean	Std. devn.
10	1.03	1.03	1.02	1.00	1.02	1.02	0.025
8	0.89	0.89	0.87	0.88	0.86	0.89	0.019
6	0.75	0.77	0.75	0.76	0.78	0.76	0.025
4	0.61	0.62	0.60	0.63	0.61	0.61	0.017
2	0.45	0.46	0.45	0.46	0.49	0.46	0.033
DMF control	0.32	0.31	0.35	0.32	0.31	0.32	0.033
Cell blank	0.32	0.32	0.35	0.32	0.32	0.33	0.025

solutions prepared by dissolution of magnesium metal in hydrochloric acid. The instrument was calibrated before and during each set of determinations. The calibration curves were the same whether citrate buffer was present in the standards or not.

RESULTS AND DISCUSSION

Table 1 shows the amount of Mg^{2+} released from freshly prepared yeast cells by the action of nystatin at concentrations ranging from 2 to 10 IU/ml. A linear relationship between dose and response was observed over this range (correlation coefficient 0.998). Table 2 shows the corresponding data for yeast inocula stored under liquid nitrogen. The relationship is again linear (correlation coefficient 1.00). The reproducibility is satisfactory and compares favourably with that reported for other assay methods for the polyene antibiotics.[18] Use of a "reagent" yeast significantly improves the reproducibility (Table 2). For an assay to be precise and accurate the dose-response curve is of vital importance,[7,8] so knowledge of the factors affecting it is critical. In view of this, factors such as the growth phase of the cells, temperature of growth of the cells, temperature of incubation with antibiotic, and contact time, were investigated. The conditions outlined in the procedure are those found to be optimal.

The assay of polyene antibiotics by measurement of the Mg^{2+} leaked after interaction with antibiotic is therefore feasible over the range 2–10 IU/ml. The assay time is 30 min (excluding solution preparation time *etc.*) and thus the proposed assay can be regarded as rapid. The widely used agar-plate diffusion assay[7,8] for this group of antibiotics takes 16–18 hr and is operable over the range 20–80 IU/ml with a reproducibility of *ca.* 5%.[8] A recent comparative study[18] of the procedures at present available for the polyene group of antibiotics showed that the bioassay system reported in this paper is acceptable in terms of speed, reproducibility and sensitivity. Most importantly, it does not require the growth of a special yeast nor does it require the use of uncommon laboratory equipment. It therefore appears a worthwhile alternative to more elaborate[8,9,16] or expensive[9] techniques. There appears to be no reason why Mg^{2+}-free formulations of this antibiotic could not be assayed by the technique reported here.

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DETERMINATION OF THIOSULPHATE IN THE PRESENCE OF DITHIONITE AND SULPHITE

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Summary—To determine thiosulphate in the presence of dithionite and sulphite, iodine dissolved in potassium bromide solution is used to oxidize thiosulphate to tetrathionate, and dithionite and sulphite to sulphate. The tetrathionate generated from the thiosulphate is then oxidized with potassium bromate–potassium bromide solution in the presence of hydrochloric acid. The bromine consumption of the tetrathionate is measured by titration of the excess of bromine with sodium thiosulphate after the addition of potassium iodide. For each equivalent of iodine used to determine thiosulphate by the Wollak method, fourteen equivalents of bromine are used to determine thiosulphate by this method.

Dithionites are labile compounds which undergo rapid disproportionation in aqueous solution, but in crystalline state the disproportionation is much slower. [1–4]

$$2S_2O_4^{2-} + H_2O \rightarrow 2HSO_3^- + S_2O_3^{2-}$$

$$2Na_2S_2O_4 \rightarrow Na_2S_2O_5 + Na_2S_2O_3$$

Because of these disproportionation reactions even solid dithionite samples always contain sulphite and thiosulphite. For this reason dithionite samples can be analysed accurately only by determination of all three species.

Dithionite is oxidized to sulphate by iodine and bromine.[5,6] As is well known, thiosulphate is oxidized to tetrathionate by iodine[7] but to sulphate by bromine.[8]

$$S_2O_4^{2-} + 4H_2O + 3I_2 \rightarrow 2SO_4^{2-} + 8H^+ + 6I^-$$

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

$$S_2O_3^{2-} + 5H_2O + 4Br_2 \rightarrow 2SO_4^{2-} + 10H^+ + 8Br^-$$

According to Wollak,[9,10] for the determination of thiosulphate in the presence of dithionite and sulphite an aliquot of the sample solution is treated with a calculated amount of iodine, then excess of sulphite is added which reacts with the tetrathionate quantitatively in neutral solution.

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-}$$

The excess of sulphite is then masked with formaldehyde and the thiosulphate is titrated with iodine. The accuracy of this method is slightly limited because the amount of thiosulphate actually titrated is only 50% of the original thiosulphate content of the sample.

Szekeres[8] used two aliquots for the determination of thiosulphate in dithionite solution. To the first aliquot an excess of iodine was added and the surplus was titrated with thiosulphate. The second aliquot was treated with bromine (potassium bromate–potassium bromide) solution, and the excess of bromine was determined by addition of potassium iodide and titration with thiosulphate solution. As shown in Table 1, the thiosulphate content can be calculated from the difference in the iodine and bromine consumption. In this method a source of error arises from the need to use two aliquots, but theoretically this method is fourteen times as sensitive as Wollak's method.

Szekeres noted that dithionite is quantitatively converted into sulphite and elemental sulphur in the presence of hydrochloric acid.[8]

$$2S_2O_4^{2-} \rightarrow SO_3^{2-} + S_2O_5^{2-} + S$$

In the presence of a limited amount of hydrochloric acid thiosulphate does not decompose. If the sulphite is masked with formaldehyde, the thiosulphate can be titrated with iodine. In theory, this method would be twice as sensitive as Wollak's method.

A more sensitive method for the determination of thiosulphate in the presence of dithionite and sulphite is the one described in this paper. The principle is as follows.

The sample solution is oxidized with iodine. The excess of iodine is titrated with dilute sodium hydrogen sulphite solution. After these operations, the solution contains sulphate and tetrathionate. Then the resulting tetrathionate is oxidized with bromate–bromide solution in the presence of hydrochloric acid.

$$S_4O_6^{2-} + 7Br_2 + 10H_2O \rightarrow 4SO_4^{2-} + 20H^+ + 14Br^-$$

Iodine dissolved in concentrated potassium bromide solution is used for the oxidation of the thiosulphate–dithionite solution. Iodine dissolved in potassium iodide solution or in ethanol cannot be used, because

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Table 1. Ratio of equivalents of reagent to moles of determinand

Procedure Reagent	*A* I	*B* Br	*D* HCHO/I	*H* I in KBr/Br
$S_2O_4^{2-}$ (x)	6	6	4	—
$S_2O_3^{2-}$ (y)	1	8	1	7
SO_3^{2-} (z)	2	2	—	—

bromine would react with the potassium iodide or with the ethanol.

Ten dithionite–sulphite–thiosulphite mixtures have been analysed according to Szekeres[8] and according to the method in this paper. The dithionite content has also been determined, according to the well-known formaldehyde method of Wollak.[9] It was found that the maximum difference between the thiosulphate results obtained by the two methods was 2.5 mg. Thus the inaccuracy of the three titrations taken together was equivalent to about 0.2–0.25 ml of 0.1*N* iodine.

The basis of the calculation is the iodine and bromine consumption, as can be seen in Table 1.

For the calculations the number of ml of 0.1*N* titrant used in procedures *A*, *B*, *D* and *H* are inserted in place of the corresponding letter in the following formulae, to give mmole of the species denoted. The letters *A*, *B* and *D* refer to procedures already given these labels elsewhere by Szekeres, and *H* to the one in this paper.

$$x = \frac{7D + A - B}{280}; \quad y = \frac{B - A}{70};$$

$$z = 0.05A - 0.05D - \frac{7D + A - B}{280}; \quad y = \frac{H}{70}$$

The data presented in Table 2 show the amounts of thiosulphate determined in the samples by the two methods and also the amounts of dithionite and sulphite found in the samples.

In order to prove that the method described is suitable for the determination of thiosulphate in dithionite–thiosulphate–sulphite mixtures, a determination was performed on standardized sodium thiosulphate instead of a dithionite mixture, according to procedures *A*, *B*, *D* and *H*. Results near to the calculated amount of sodium thiosulphate were obtained.

EXPERIMENTAL

Reagents

Iodine solution (0.1*N*). Containing 60 g of acetic acid per litre.

Potassium bromate solution (0.01667*M*: 0.1*N*). Containing 50 g of potassium bromide per litre.

Iodine in potassium bromide solution. Dissolve 500 g of potassium bromide in 500 ml of water, add 6.5 g of iodine and stir for several hours. Dilute to 1000 ml and filter through a sintered-glass filter.

Sodium hydrogen sulphite solution, 0.025*M*.

Sodium thiosulphate solution, 0.1*N*.

Sample solution

Weigh 0.7–1.0 g of sodium dithionite–thiosulphate–sulphite mixture and dissolve it in oxygen-free water in a 200-ml standard flask. Dilute to volume, mix, and use 10-ml aliquots from the solution within 5 min. Cloudy solutions should be discarded and fresh ones made.

From each sample solution take eight aliquots, two aliquots each for procedures *A*, *B*, *D*, and *H*.

Procedure A

Place in a glass-stoppered flask 20 ml of water and 20.0 ml of 0.1*N* iodine. Add 10.0 ml of sample solution. After 2–3 min titrate the excess of iodine with 0.1*N* sodium thiosulphate. The consumption is *A* ml.

Table 2

$S_2O_3^{2-}$, *mg* Procedures *A*, *B*	$S_2O_3^{2-}$, *mg* Procedures *H*	Difference $S_2O_3^{2-}$, *mg*	$S_2O_4^{2-}$, *mg* Procedures *A*, *B*, *D*	SO_3^{2-}, *mg* Procedures *A*, *B*, *D*
35.73	37.18	1.35	17.21	4.32
27.52	29.68	2.16	18.53	0.14
21.20	21.92	0.72	18.74	3.12
10.64	11.67	1.03	18.24	3.80
39.31	39.84	0.53	16.45	5.64
6.54	7.44	0.90	13.16	9.57
47.87	47.92	0.05	17.68	2.87
5.57	5.63	0.06	14.89	5.17
54.99	54.77	0.22	15.09	5.05
26.93	27.74	0.81	14.28	3.77

Procedure B

Place in a iodine-flask 50.0 ml of 0.01667*M* potassium bromate solution (containing bromide). Add 10.0 ml of sample solution. Quickly add 10 ml of concentrated hydrochloric acid and allow to stand for 30 min. Add 50 ml of water and 1 g of potassium iodide and after 2–5 min titrate with 0.1*N* sodium thiosulphate. The consumption is *B* ml.

Procedure D

Place in a glass-stoppered flask 10 ml of formaldehyde solution and 10 ml of water. Add 10.0 ml of sample solution. After 30 min add 50 ml of water and 20.0 ml of 0.1*N* iodine. Titrate with 0.1*N* sodium thiosulphate after 2–5 min. The consumption is *D* ml.

Procedure H

Place in an iodine-flask 25 ml of iodine–potassium bromide solution. Add 10.0 ml of sample solution. If the resulting solution is colourless, add more iodine–potassium bromide solution. Add 0.025*M* sodium hydrogen sulphite dropwise from a burette until the yellow solution becomes colourless. Add 50.0 ml of the 0.01667*M* potassium bromate solution (containing bromide) and 10 ml of concentrated hydrochloric acid. After 30 min add 1 g of potassium iodide and titrate with 0.1*N* sodium thiosulphate. The consumption is *H* ml.

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EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM, RHODIUM AND IRIDIUM

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Summary—Platinum, iridium and rhodium in mixtures are determined sequentially, with rubeanic acid, tin(II) chloride and tin(II) iodide respectively. The working ranges (in μg) are: Pt 7–100, Rh 7–70, Ir 7–30.

Spectrophotometric determination of platinum metals in the presence of one another is subject to numerous difficulties, mainly caused by the similarity in the properties of the metals. Usually, a separation is required, especially of rhodium and iridium. The commonest method for their separation is extraction comcombined with masking or precipitation reactions.[1–9] After the extraction it is usual for the organic solvent to be evaporated, the residue mineralized and the metals determined by the tin(II) methods.[1–7] An alternative[8,9] is to determine the metal ions in the form in which they were extracted.

In the present paper a method is suggested which simplifies the analytical procedure and permits determination of platinum, iridium and rhodium in the same solution.

EXPERIMENTAL

Reagents

Rubeanic acid. A 0.1% solution in ethyl alcohol.

Ethanolic hydrochloric acid. A 1:1 v/v mixture of concentrated hydrochloric acid and 96% alcohol, prepared fresh every day.

Stannous chloride. A 1*M* solution in concentrated hydrochloric acid.

Stannous chloride solution, 33%. Dissolve *x* g of $SnCl_2 \cdot 2H_2O$ in 3*x* ml of a 1:2 v/v mixture of concentrated hydrochloric acid and water.

Potassium iodide solution, 40%.

Standard solutions. Chloroplatinic acid (Pt 14 g/l.), chlororhodic acid (Rh 7 g/l.) and chloroiridic acid (Ir 2 g/l.).

The organic reagents utilized were distilled before use.

Procedure

Two samples (A and B) containing platinum(IV), rhodium(III) and iridium(III) as their chlorides were placed in separating funnels, then with constant swirling additions were made of 5 ml of ethanolic hydrochloric acid and 4 ml of rubeanic solution. After 20 min the pink platinum complex was extracted with 10 ml of tributyl phosphate (TBP). The extracts were filtered into 25-ml standard flasks and made up to volume with TBP; the absorbances were measured at 510 nm against a reagent blank.

The aqueous layers, containing the rhodium and iridium, were shaken with 10 ml of hexane. The aqueous phases were transferred to small evaporating dishes and evaporated on a water-bath almost to dryness. The residues were dissolved in a small quantity of hydrochloric acid. Then hydrochloric acid was added to sample A until its concentration was 6*M*, followed by 2 ml of 3% hydrogen peroxide to oxidize iridium(III). After heating on a water-bath to 90° and decomposition of the excess of peroxide, the solution was cooled, transferred to a separating funnel and shaken with 5 ml of TBP. The organic layer, containing iridium in TBP, was discarded and the aqueous phase was shaken with 10 ml of n-hexane. The hexane layer was discarded and the aqueous phase (containing rhodium) was transferred to a 25-ml standard flask; 2 ml of 1*M* stannous chloride were added and the flask was heated for 10 min on a boiling water-bath, then cooled. Then 2 ml of 33% stannous chloride solution were added, the solution was diluted to the mark with water and the absorbance was measured at 475 nm against a reagent blank.

For determination of iridium, sample B was transferred to a separating funnel, 2 ml of 1*M* stannous chloride were added and mixed well, then after 10 min (not longer) the rhodium was extracted with 10 ml of ethyl acetate. The organic phase was discarded, and the aqueous layer (containing iridium) was transferred to a 25-ml standard flask. Hydrochloric acid was added, until its concentration was 1.3*M*, followed by 5 ml of 40% potassium iodide solution. The mixture was heated for 10 min on a boiling water-bath and then cooled. After addition of 2 ml of 33% stannous chloride solution and dilution to the mark with water the solution was heated for 3 min on a water-bath and cooled rapidly. The absorbance was measured at 446 nm against a reagent blank. Calibration curves were prepared under the same experimental conditions.

Table 1. Interference study on the determination of 28 μg of Pt(IV)

Foreign ion	Tolerance limit, μg
Co	500
Ni	1000
Fe	500
Pd	15

Table 3. Number of extractions necessary for separation of Pt from 41 μg of Rh and 28 μg of Ir

Pt added, μg	Pt found, μg	
	1 extn.	2 extns.
85.7	83.5	83.5
42.8	42.5	42.5

DISCUSSION

Rubeanic acid was used for the determination of platinum. To prevent precipitation of the complex a 1:1 mixture of concentrated hydrochloric acid and 96% ethyl alcohol was used. This enabled us not only to improve the sensitivity (to 0.28 μg/ml), but also to increase the time for which the complex remained stable (to 2 hr) and to widen the range of platinum determinations relative to methods described previously.[10,11]

An important advantage of our method is that Pt(IV) may be determined directly in a solution also containing rhodium and iridium. The Pt(IV)–rubeanic acid complex is easily extracted with TBP, and this extraction is used for separating platinum from the other ions in the solution.

Rhodium and iridium were determined by means of stannous chloride and iodide respectively. Stannous halides are often used to determine platinum metals, because they react instantly and the reactions are highly sensitive. The stability of the iridium complexes increases in the order chloride < bromide < iodide. For rhodium the order is the opposite. However, all the platinum metals react with stannous halides, so when one of them is to be determined, the others must be removed.

Hence we needed two samples (after prior removal of platinum). In one, to determine rhodium with tin(II) chloride,[12] the iridium(III) was oxidized to iridium(IV), which was then removed by extraction with TBP.[4] In the other, the rhodium, after complexation with stannous chloride in concentrated hydrochloric acid, was extracted with ethyl acetate.

We have found that the rhodium is fully complexed even at room temperature and that during the period (10 min) necessary for this, only the rhodium reacts with the stannous chloride.

In the present study platinum was determined within the range from 7 to 100 μg, rhodium from 7 to 70 μg, and iridium from 7 to 30 μg. Solutions were taken in which the Pt, Rh and Ir were in various proportions. In platinum metal alloys base metals are usually absent, but may occur in various platinum metal solutions. The most frequent contaminating ions are Fe(III), Co(II), Ni(II) and Cu(II). We investigated the interference of these and of Pd(II) in the separation and determination of Pt(IV), Rh(III) and Ir(III).

All these ions interfere in the platinum determination (Table 1) and the lowest tolerance limits are found for Pd and Cu. These metals should be absent in the determination of Pt with rubeanic acid; the other metals investigated may be present, if below the tolerance limit.

Using atomic absorption, we found that when 60 μg of each were present, only about 95% of the Fe(III), Ni(II) and Co(II) was extracted simultaneously with Pt(IV) into TBP.

The incomplete extraction in the case of cobalt and nickel is probably due to non-quantitative reaction with rubeanic acid under the highly acidic conditions necessary for extraction and determination of Pt(IV). Even use of a larger excess of rubeanic acid does not improve the results. The amount of Fe(III), Co(II) and Ni(II) left in the aqueous phase interferes in the determination of Ir and Rh, as also do Pd(II) and Cu(II).

Our method is therefore restricted in use to determination of Pt, Ir and Rh in certain alloys (especially those of low Rh content). These alloys are most conveniently dissolved by chlorination in the presence of sodium chloride.

A single extraction is adequate for separation of iridium from rhodium (Table 2) and of platinum (Table 3).

The determination results are collected in Table 4. The largest error is encountered when the rhodium content is far higher (>70 μg) than that of iridium (<10 μg).

The method suggested is far simpler and shorter than the methods cited at the beginning of the paper.

Table 2. Number of Ir extractions necessary for satisfactory determination of Rh

Rh added, μg	Rh found, μg			Ir added, μg
	1 extn.	2 extns.	3 extns.	
28.2	28.2	28.2	26.8	24.3
42.2	42.2	45.1	45.1	40.6
56.3	53.5	52.1	49.3	24.4
70.4	70.4	81.0	84.5	30.0

Table 4. Results of analysis of mixtures of Pt, Rh and Ir

Taken, μg			Found, μg		
Pt	Rh	Ir	Pt	Rh	Ir
14.3	14.1	16.2	14.3	14.2	16.2
			14.2	14.2	16.1
			14.2	14.1	16.1
			21.4	27.6	19.9
21.4	28.2	20.3	21.3	26.9	19.5
			21.3	26.6	19.2
			28.2	42.2	14.2
28.6	42.2	16.2	28.2	42.1	16.1
			28.1	42.0	16.1
			35.2	81.6	13.3
35.7	84.5	12.2	34.9	80.0	13.1
			34.9	79.6	13.0
			17.0	29.7	19.7
17.1	28.2	20.3	17.0	29.7	19.7
			17.0	29.6	19.4
			7.1	70.4	23.2
7.1	70.4	24.3	7.1	70.4	23.0
			7.1	70.1	22.6
			84.0	42.0	6.3
85.7	42.2	6.5	83.5	40.8	6.2
			83.1	40.2	6.2
			96.9	55.0	27.9
100.0	56.3	28.4	96.6	53.6	27.5
			96.2	53.0	27.4
			42.6	35.1	4.1
42.8	35.2	4.2	42.5	34.8	4.1
			42.5	34.5	4.1

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A RAPID METHOD FOR THE ESTIMATION OF GLUTAMIC ACID WITH CHLORAMINE-T

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Summary—Chloramine-T (added in excess) oxidizes glutamic acid in various solvent media and the reaction is rapid and stoichiometric with a 4-electron change in buffers of pH 1–6, in 0.01*M* sulphuric and perchloric acids and in 0.1*M* hydrochloric acid. A back-titration procedure using a pH-4 buffer or 0.1*M* hydrochloric acid as reaction medium has been developed. *p*-Toluenesulphonamide and a nitrile have been identified in the reaction products. The effect of other species on the oxidation has been investigated.

Chloramine-T (CAT) has been used for the oxidation of a variety of organic and inorganic substrates[1–5] and the oxidation mechanisms have been kinetically investigated.[6–10] During investigation of oxidation of some amino-acids such as serine, glutamine, hydroxyproline and glutamic acid by CAT we observed that glutamic acid undergoes rapid oxidation in buffers of pH 1–6 and sulphuric, perchloric and hydrochloric acid media when an excess of CAT is added, with a 4-electron change; the reaction was found to be fastest in 0.1–1.0*M* hydrochloric acid. However, when the glutamic acid is in excess the reaction is too slow to be useful for a direct titration, and a back-titration procedure is necessary and has been developed.

Glutamic acid is a non-essential amino-acid present in all complete proteins. The monosodium salt, L(+) sodium glutamate, finds extensive commercial use as a flavour intensifier. Glutamic acid itself is used in medicine and biochemical research, and as a salt substitute and dietary supplement. A survey of the literature shows that there are few methods for assay of the compound, except the general methods for estimation of amino-acids. The procedure described here is rapid and accurate, and is applicable in the presence of various organic compounds.

Mixtures of glutamic acid with glutathione or cysteine can be analysed for both components by determining the thiol by direct titration and the sum of the two components by back-titration.

EXPERIMENTAL

Reagents

Recrystallized glutamic acid was used. Its purity was checked by non-aqueous titration with perchloric acid.[11] Chloramine-T was purified by the method of Morris *et al.*[12] An approximately 0.1*N* solution was prepared and standardized by the iodometric method.[13] All other reagents were of accepted grades of purity. Thrice-distilled water was used for preparing the solutions.

Preliminary studies

Known amounts of glutamic acid solution in various solvents were added to a known and excessive volume of CAT in an iodine-flask at room temperature (25 ± 3°). The reaction mixture was set aside for various intervals of time, with occasional shaking. Then the excess of CAT was determined by iodometric back-titration. Table 1 gives a typical set of results for the extent of oxidation of glutamic acid in 5 min by an excess of CAT. It is seen that the oxidation is stoichiometric in buffer media of pH 1–6, 0.01*M* sulphuric and perchloric acids and 0.1*M* hydrochloric acid. The oxidation of acid is sluggish at pH > 6 and in 0.01–1.0*M* sulphuric or perchloric acid, but rapid at hydrochloric acid concentrations above 0.1*M*. The reaction is complete in 2 min in pH-4 buffer or 0.1*M* hydrochloric acid.

Recommended procedures

Glutamic acid. Take a sample containing up to 1.0 mmole of glutamic acid, and dissolve it in (*a*) pH-4 acetate buffer or (*b*) water. Add (*a*) the buffered solution to 25 ml of 0.1*N* CAT, or (*b*) the aqueous solution to 25 ml of 0.1*N* CAT plus 2 ml of 6*M* hydrochloric acid. After about 2 min, add 20 ml of 10% potassium iodide solution and 10 ml of 2*N* sulphuric acid. Titrate the liberated iodine with 0.1*N* sodium thiosulphate solution. Run a blank with CAT solution alone.

The amount (x mg) of glutamic acid is given by

$$x = 36.78y(V_1 - V_2)$$

where y is the normality of the sodium thiosulphate, V_1 is the blank titration and V_2 is the volume of sodium thiosulphate used to titrate the excess of CAT.

Glutathione and glutamic acid. (*a*) Prepare a sample solution and to an aliquot of it add 2 ml of starch–

Table 1. Extent of oxidation of glutamic acid with chloramine-T

Medium	CAT used, *mole* / Glutamic acid taken, *mole*	Medium	CAT used, *mole* / Glutamic acid, *mole*
1.00*M* H_2SO_4	0.474	pH 1.0	2.009
0.10*M* H_2SO_4	1.942	pH 2.0	2.001
0.01*M* H_2SO_4	2.000	pH 3.0	2.001
1.00*M* $HClO_4$	0.616	pH 4.0	2.001
0.10*M* $HClO_4$	1.980	pH 5.0	2.001
0.01*M* $HClO_4$	2.000	pH 6.0	1.975
1.00*M* HCl	2.000	pH 7.0	1.390
0.10*M* HCl	2.000	pH 8.0	0.734
0.01*M* HCl	1.968	1.00*M* NaOH	0.010
		0.10*M* NaOH	0.010
		0.01*M* NaOH	0.010

Glutamic acid taken: 0.2 mmole. Time: 5 min.
CAT taken: 2.0 mmole. Temperature: 25°C.

iodide indicator and enough 2*N* sulphuric acid to make the overall acid concentration approximately 0.04*N*. Titrate slowly, with stirring, with 0.001*N* CAT, to the appearance of a pale blue colour.[14] The amount of glutathione present (mg) is 307.3 *VN*, where *V* and *N* are the volume (ml) and normality of the CAT.

(*b*) Take an identical aliquot of sample in an iodine-flask and adjust the pH to 5 with acetate buffer. Add 50 ml of 0.1*N* CAT. Leave aside for 30 min. Add 10 ml of 2*N* sulphuric acid and 10 ml of 20% potassium iodide solution and titrate the liberated iodine with standard thiosulphate solution (V_1 ml). Do a blank titration with the same volume of CAT (V_2 ml of thiosulphate).

The amount of glutamic acid present (mg) is 36.78 y ($V_2 - V_1 - 10VN/y$).

Cysteine and glutamic acid. Use the procedure for the glutathione/glutamic acid mixture, but with 0.2*N* sulphuric acid for the direct titration[15] and pH-1 buffer for the back-titration.

Many commercial pharmaceutical preparations contain glutamic acid as a major component, along with riboflavin and nicotinamide. The latter do not interfere in the determination of the glutamic acid when hydrochloric acid is used as the reaction medium.

The following compounds (at the levels shown in brackets) interfere in either reaction medium: folic acid (1.7 mg); calcium gluconate (0.4 mg); calcium

Table 2. Estimation of glutathione and glutamic acid in mixtures

Glutathione, direct titration with CAT		Glutamic acid, back-titration	
Taken, *mg*	Found, *mg*	Taken, *mg*	Found, *mg*
8.72	8.7	7.87	7.9
13.08	13.0	11.81	11.9
17.40	17.4	15.74	15.7
30.24	30.3	30.39	30.4
40.32	40.3	40.52	40.7
50.40	50.4	50.65	50.6

Table 3. Estimation of cysteine and glutamic acid in mixtures

Cysteine, direct titration with CAT		Glutamic acid, back-titration	
Taken, *mg*	Found, *mg*	Taken, *mg*	Found, *mg*
10.01	9.9	10.12	10.1
15.63	15.6	15.48	15.5
20.02	20.0	20.24	20.1
30.09	30.1	30.06	30.2
31.26	31.3	31.56	31.6
40.12	40.2	40.08	40.0
50.15	50.0	50.10	50.6

Table 4. Estimation of glutamic acid in presence of riboflavin and nicotinamide

Composition of the mixture, *mg*			Glutamic acid found, *mg*
Riboflavin	Nicotinamide	Glutamic acid	
5.13	5.15	12.31	12.4
5.00	5.00	20.04	20.0
10.26	10.30	24.62	24.6
15.39	15.45	36.93	36.7
20.52	20.60	49.24	49.2
25.65	25.75	61.55	61.6

pantathenate (2.3 mg); pyridoxine hydrochloride (1.0 mg); thiamine hydrochloride (1.7 mg); glycine (1.0 mg). Typical results are shown in Tables 2–4.

Note. In our earlier paper on glutathione,[14] it was stated that glutamic acid may not interfere in the back-titration procedure for glutathione. This statement arose from an oversight by the authors and is obviously incorrect.

RESULTS AND DISCUSSION

Determinations of 2.5–75 mg of glutamic acid were achieved in both pH-4 buffer and 0.1*M* hydrochloric acid medium with an average error of 0.1% and a maximum error of 0.5%.

Detailed investigation of the system brought out the following facts

(*i*) The stoichiometry of the oxidation can be represented by

$$HOOC(CH_2)_2CH(NH_2)COOH + 2RNClNa \rightarrow$$
$$2RNH_2 + HOOC(CH_2)_2CN + CO_2 + 2NaCl$$

where $R = CH_3C_6H_4SO_2$.

The presence of *p*-toluenesulphonamide among the reaction products was detected by paper chromatography. Benzyl alcohol saturated with water was used as solvent, 0.5% vanillin in 1.0% hydrochloric acid solution in ethanol as spray reagent ($R_F = 0.91$). The presence of nitrile in the reaction product was detected by its colour reaction with hydroxylamine and ferric chloride.[16]

(*ii*) Ions such as K^+, Ba^{2+}, Zn^{2+}, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_4^- have no influence on the rate of oxidation of the amino-acid.

(*iii*) Sodium chloride (up to 0.5 mole) has no influence on the rate.

(*iv*) The stoichiometry is unaffected by the order of addition of the oxidant and glutamic acid.

(*v*) The reaction rate is retarded in sulphuric and perchloric acid media of high concentrations although stoichiometric oxidation is complete within 30 min.

(*vi*) The oxidation mechanism does not involve the disproportionation of chloramine-T into dichloramine-T and *p*-toluenesulphonamide suggested by Higuchi *et al.*[17]

Interferences

Any species oxidized by excess of CAT will interfere.

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ANALYTICAL DATA

DISSOCIATION CONSTANTS OF THYMOLPHTHALEXONE

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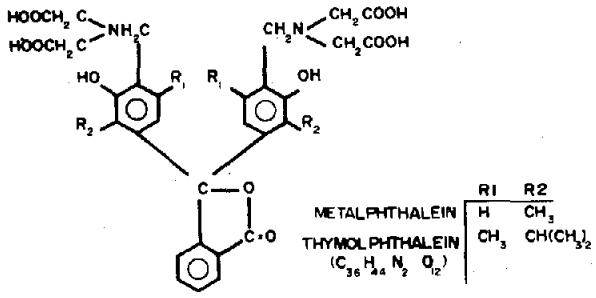
Summary—For the dissociation constants of thymolphthalexone the following values have been found: $pK_3 = 7.03 \pm 0.02$, $pK_4 = 8.05 \pm 0.09$ (by potentiometric titration), $pK_5 = 10.83 \pm 0.10$, $pK_6 = 12.99 \pm 0.11$ (by spectrophotometry). They were determined at $I = 0.4$ and at 25°.

In the course of preparation of a comprehensive study of complexometric indicators[1] the protonation constants of thymolphthalexone have been investigated. Bezdeková and Buděšinský[2] give pK values of 7.4 and 12.3 for two successive dissociation steps of this indicator. These values are doubtful because they differ by nearly 5 pK units, and from the structure of the compound and the values for metalphthalein[3] (2.20, 2.90, 6.97, 7.83, 11.39, 12.01) which is closely related to thymolphthalexone, it would be expected that in the pH range 6–14 there should be four dissociation equilibria. Because thymolphthalexone is a widely used complexometric indicator,[1,4] knowledge of its protonation constants is of importance for its proper use.



	R1	R2
METALPHTHALEIN	H	CH_3
THYMOLPHTHALEIN $(C_{36}H_{44}N_2O_{12})$	CH_3	$CH(CH_3)_2$

EXPERIMENTAL

Procedure

For spectrophotometric determination of the constants, absorption curves (330–800 nm) were prepared for $5 \times 10^{-5}M$ aqueous solutions of thymolphthalexone in buffers and sodium hydroxide solutions ranging in pH from 7 to 14.5.[5] To all solutions, except those more than 0.4M in sodium hydroxide, sodium sulphate was added to provide a constant ionic strength of 0.4. In acidic solutions (pH < 7) no absorption changes were observed. In all the solutions investigated only one maximum was found, at 605 nm.

Because in the pH range from 7 to 9 the absorbance and its changes are small, potentiometric measurements were used for determination of the constants. Solutions containing 1.95×10^{-4} mole of the disodium salt of thymolphthalexone in 150 ml were titrated with 0.098M sodium hydroxide (Fig. 1). All measurements were made at 25 ± 1° and the solutions were deaerated with argon to avoid interference by carbon dioxide.

RESULTS

The dependence of absorbance on pH (Table 1) is identical with that shown by Bezdeková and Buděšínsky.[2] If it is assumed that in the pH range 10–13.5 only one protonation equilibrium exists, the graphical procedure leads to the value pK = 12.35, in good agreement with the previously reported

Table 1. Spectrophotometric determination of dissociation constants of thymolphthalexon

pH*	Absorbance	pK calc. from eq. (1)	pK calc. according to Albert and Serjeant[6]
8.00–8.90	0.060		
9.33	0.080	10.9	10.76
9.47	0.095	10.9	10.62
9.74	0.120	11.0	10.63
10.10	0.155	11.1	10.75
10.48	0.205	11.3	10.85
10.85	0.250	11.6	11.03
10.94	0.270	11.6	11.02
11.10	0.310	11.7	10.98
11.23	0.345	11.7	10.88
11.55	0.430	11.9	10.76
12.31	0.640	12.3	13.23
12.66	0.820	12.4	12.97
12.85	0.930	12.5	12.89
12.97	0.960	12.5	12.94
13.36	1.070	12.7	13.06
13.66	1.180	12.7	13.01
13.85	1.245	12.5	12.85
14.0–14.58	1.310		

* For solutions more alkaline than pH 12, the basicity was calculated from the function H^5.

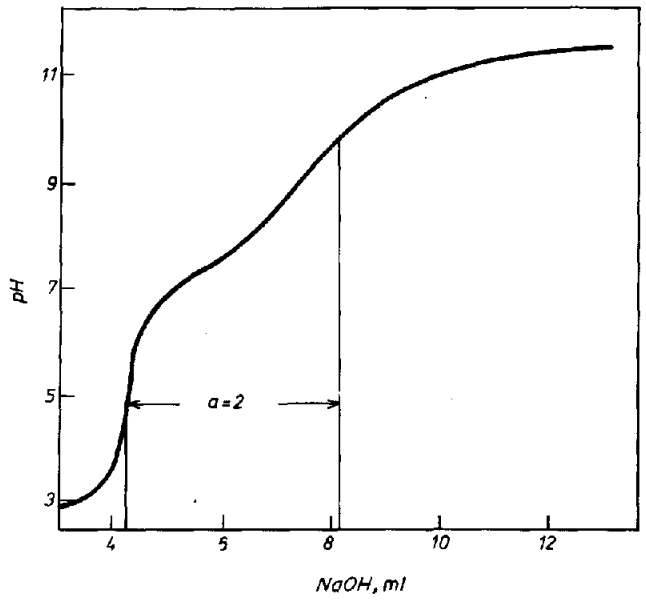


Fig. 1. Titration curve of 1.95×10^{-4} mole of thymolphthalexone with 0.098*M* NaOH (uncorrected for acid impurities in the sample).

value.[2] If more detailed calculations are performed, based on the equation

$$pK = pH + \log \frac{A_I - A}{A - A_{II}} \qquad (1)$$

where A_I and A_{II} are the absorbances of the basic and acidic forms respectively, and A is the absorbance at the given pH, the computed values of pK change systematically (Table 1, column 3), which clearly indicates that the assumption that there is only one protonation equilibrium is wrong. It was therefore assumed that two overlapping equilibria occur, and the individual values were calculated by using the program given by Albert and Serjeant,[6] translated into ALGOL IV. The calculated values (Table 1, column 4) are 10.83 ± 0.10 and 12.99 ± 0.11, respectively (95% confidence) and correspond to deprotonation of the two NH^+ groups arising from the zwitter-ion.

The potentiometric titration curve (Fig. 1) indicates the pH changes (in the region 6–9) corresponding to deprotonation of the two phenolic groups. A further buffer region at higher acidities, which cannot be investigated potentiometrically with sufficient precision, corresponds to the protolytic reactions of the carboxylic groups.

The protolytic equilibria involving the –OH groups were calculated from the titration curve (Fig. 1) by using the program presented by Albert and Serjeant,[6] translated into ALGOL IV. The pK values obtained are 7.03 ± 0.02 and 8.05 ± 0.09 (95% confidence).

The four values obtained for the protonation equilibria are similar to those found for metalphthalein. The two remaining constants are of less importance for complexometric titrations because thymolphthalexone is commonly used only at pH > 9.

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OXIMES AS SPECTROPHOTOMETRIC REAGENTS—A REVIEW

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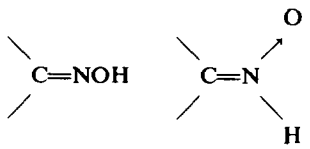
Summary—The uses of oximes as spectrophotometric reagents since 1953 are reviewed.

The name oxime is an abbreviation of oxy-imine, >C=NOH. Oximes are derived from aldehydes or ketones by replacement of the oxygen atom of the aldehyde group (aldoximes) or the keto group (ketoximes). The oxime group is amphiprotic in nature, having a slightly basic nitrogen atom and a mildly acidic hydroxyl group.

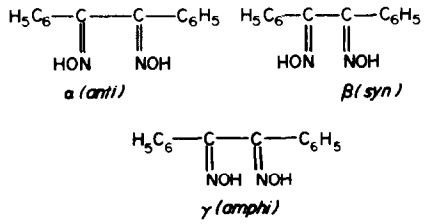
Two main structures (A) and (B) are proposed for the oxime group, with evidence for an equilibrium between them.[1]



(A) (B)

The neutron diffraction work[2] on dimethylglyoxime established the presence of O–H bonds, favouring structure (A). Oximes are usually associated[2–10] in the solid state by hydrogen-bonding, O–H ... N.

Isomerism in the oximes was first described by Werner.[11] Owing to the restricted rotation around double bonds the oximes exhibit geometrical isomerism. Occurrence of two[12] isomers in monoximes and three[13] in dioximes may be visualised as below:



α (anti) β (syn)

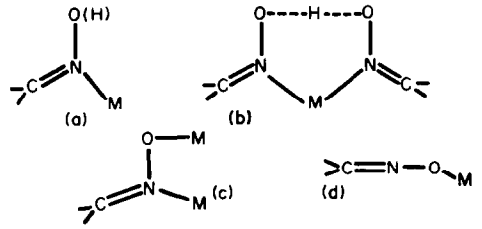
γ (amphi)

The isomers are usually identified by chromatographic or spectroscopic methods. TLC has successfully been used by Toul *et al.*[13a] to separate and identify benzil-α-monoxime, furilmonoxime, furil dioxime and their isomers, and dimethyl monoxime in dimethylglyoxime. Soules *et al.*[14] separated and identified various isomers of 2,2′-pyridiloximes.

It is interesting to note that the different geometrical isomers for the *vic*-dioximes have been isolated only in the aromatic series. There is little evidence that the β(syn)- or γ(amphi)-isomers exist in either aliphatic or alicyclic series[15] of *vic*-dioximes.

Modes of bonding

The oxime group has two donor atoms, N and O, and may co-ordinate to a metal atom through either or both, thus acting as unidentate or bidentate, respectively. The following structures may arise from the different modes of co-ordination of an oxime.



(a) (b) (c) (d)

(Oximes can react either as such or in the form of the conjugate base; this is indicated by putting the hydrogen atom H in parenthesis.)

The structural types (*a*) and (*b*) are quite common. The type (*c*) is known in polynuclear species, whereas only a few complexes belong to type (*d*).

The mode of co-ordination of the oxime group is greatly influenced by the other group(s) present in the ligand. The oxime group may be the sole co-ordinating group present or accompanied by another donor group. On this basis the oximes may be grouped into the following main classes:

1. Simple oximes
2. *vic*-Dioximes
3. Carbonyl oximes
4. Nitrosophenols
5. Imine-oximes
6. Pyridine oximes
7. Azo-oximes
8. Hydroxyoximes
9. Amine oximes
10. Amidoximes

Structures of metal-oxime complexes

It would be pertinent at this stage to mention, in brief, structural aspects of the metal oxime complexes encountered in this text.

Simple oximes form complexes of the type $(ML_n)X$ where X represents a univalent anion and *n* the oxidation number of the metal ion. These complexes assume varying structures and stereochemistries.

Hydroxyoximes and *vic*-dioximes form square planar bis-chelates with most bivalent ions, with closed structures due to formation of additional rings by means of interligand and hydrogen bridges. Crystal structures of many of these complexes are known.

Carbonyl oximes and nitrosophenols form inner complexes of the type ML_n where L represents the deprotonated ligand. Bis-chelates are usually square planar and tris-chelates are octahedral.

Pyridine oximes, imine-oximes, amine oximes and amidoximes form complexes of varying composition and stereochemistries, governed by the properties of the central metal ion and steric requirements.

Structures of some oxime chelates have been elucidated by infrared, NMR, X-ray and magnetic measurements *etc.*[16-18]

The bis(dimethylglyoximate) chelates of a few bivalent transition metals, *e.g.*, Ni(II), Co(II), Cu(II), Pt(II) and Pd(II) have been shown to be square planar by X-ray diffraction,[19-24] infrared spectrometry[25-29] and magnetic measurements.[30-34] The presence of stable hydrogen bridges and metal $d\pi$–$p\pi$ (oxime) bonding in these complexes has been postulated.[35-38]

Cox[39] proposed a square planar structure for nickel salicyldoximate in the solid state, from X-ray measurements. A similar structure was confirmed by Lingafelter *et al.*[40,41] for the copper salicylaldoximate derivative,[42] in which the square planar units are linked through two longer Cu–O bonds.

Ward *et al.*[43] reported the synthesis of complexes of nickel halides and nitrate with *syn*-phenyl-2-pyridyl ketoxime (HL), and Sen and Malone[44,45] synthesized complexes of various metals (*e.g.*, Ni, Co, Mn, Pd, Pt, Cu, Ag and As), with this ligand. Spectral and magnetic studies indicated octahedral geometry for the Co(II), Co(III), Ni(II) and Mn(II) complexes, linear for $[Ag(HL)_2]NO_3$ and square planar for the $Pd(L)_2$ and $Au(L)Cl_2$ complexes. The electronic spectrum of [Pd(HL)(L)]Cl bears a striking resemblance to the spectrum of the square planar $[PdCl_4]^{2-}$ ion.

2-Pyridine aldoxime (HL) forms paramagnetic[46,47] octahedral nickel(II) complexes[48,49] of the type $[Ni(HL)_3]X_2$, $[Ni(HL)_2X_2]$, [Ni(HL)(L)X] and $[NiL_2]$. In the last two complexes a six-co-ordinate structure is obtained through polymerization. With palladium(II) this ligand forms[50,51] intramolecularly hydrogen-bonded [Pd(HL)L]X and *trans*-planar $[PdL_2]\cdot 2H_2O$. With copper(II), a complex of the type [Cu(HL)(L)]X is formed, which is octahedral with very weak axial co-ordination. $Cu(HL)X_2$ is polymeric, having distorted octahedral geometry.[52]

Solubility

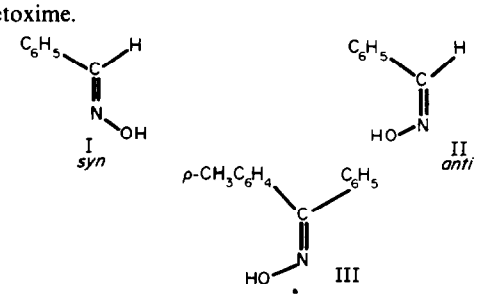
In analytical chemistry the solubilities of metal complexes are of vital importance. For instance, the analytical selectivity of dimethylglyoxime arises from the low solubilities of its complexes with nickel and palladium, whereas the corresponding complexes of all the other transition metals are quite soluble in water. The strong hydrogen-bonding of the –OH groups in the planar bis(dimethylglyoxime)nickel(II) complex makes it relatively difficult to co-ordinate water molecules and this explains its ready extractability into chloroform. In the corresponding, but non-planar, cobalt(II) complex, the –OH groups are available for bonding to solvent water molecules, thereby preventing extraction into chloroform and making possible the separation of Ni from Co.

Formation of mixed-ligand complexes also plays an important role in solubility. This is clearly illustrated by the palladium dimethylglyoxime complex, which is practically insoluble in acidic and neutral aqueous media, but is soluble in alkaline medium because the palladium central atom can bind a hydroxide ion[53] to give a negatively charged complex. The analogous nickel complex is incapable of co-ordination with hydroxide ion, even in strongly alkaline medium[54] and this is why nickel and palladium ions can be separated with dimethylglyoxime.

The differences in solubility of dimethylglyoxime complexes can also be explained in terms of unsaturation of the co-ordination spheres of the central atom.[55] Of the dimethylglyoxime complexes of the bivalent $3d^5$–$3d^{10}$ transition metal ions, only the nickel(II) complex is incapable of binding unidentate ligands (water, hydroxide ion, halide ions). This is the reason for the lower solubility of the nickel dimethylglyoxime complex in water. In the absence of additional ligands the other complexes bind water molecules, or hydroxide ions in alkaline medium, and this results in their enhanced solubilities in neutral and alkaline aqueous media.[56]

Nomenclature of the oximes

In oxime chemistry the terms *syn* and *anti* are used instead of the terms *cis* and *trans*. In the case of the aldoximes the *syn*-form is the one in which both the hydrogen atom and the hydroxyl group are on the same side; when these groups are on opposite sides, the configuration is *anti*. Thus **I** is *syn*- and **II** is *anti*-benzaldoxime. With ketoximes, the prefix indicates the spatial relationship between the first group named and the hydroxyl group. Thus **III** may be named as *syn*-*p*-tolylphenyl ketoxime or *anti*-phenyl-*p*-tolyl ketoxime.



General method for preparation

Vogel[57] has outlined the general method for the preparation of aliphatic and aromatic oximes. Preparation of monoximes is simple but that of dioximes is slightly difficult because a mixture of isomers is formed and a special procedure is employed for their separation.

Analytical applications in spectrophotometry

A large number of oximes are used as spectrophotometric reagents in analytical chemistry (Table 1).

Table 1. Spectrophotometric applications of oximes

Ions	λ_{max}, nm	ϵ, 10^3 l.mole^{-1}.cm^{-1}	pH range	Range of detn.	Extraction	M:L	Remarks	Ref.
Acenaphthenequinone monoxime								
U(VI)	400	11.2	5.5–7.0	up to 19.1 ppm	$CHCl_3$	1:2		58
Ru(III)	550	15.0	4.6–6.0	up to 6.6 ppm	$CHCl_3$	1:2	Heating for 3 hr. $\beta_2 = 1.9 \times 10^8$.	59
Pt(IV)	390	9.3	1.0–3.2	up to 23.4 ppm	$CHCl_3$	1:2	Heating for 3 hr, Pt(IV) detd. in presence of Pd(II), because Pd(II) pptes. at room temp.	60
Os(VIII)	430	5.9	6.5–8.5	up to 22.8 ppm		1:3	1.5 hr heating, 30–70% DMF-methanol.	61
Rh(III)	390	27.3	4.4–6.0	up to 3.1 ppm	$CHCl_3$	1:3	2 hr heating necessary	62
Ir(III)	385	9.1	7.0	up to 20.0 ppm	$CHCl_3$	1:3	2 hr heating necessary	63
Pd(II)	385	12.7	2.8–5.2	up to 8.9 ppm	$CHCl_3$	1:2		64
Co(II)	400	11.8	8.0–9.5	up to 6.2 ppm	$CHCl_3$	1:3		65
Cu(II)	460	8.7	6.2–8.5	up to 7.6 ppm	$CHCl_3$	1:2	Extracted into $CHCl_3$ in presence of 2 moles of pyridine.	66
Ni(II)	450	6.0	4.9–8.5	up to 12.6 ppm	$CHCl_3$	1:2		67
Fe(III)	470	2.0	2.5–9.0	up to 31.5 ppm	$CHCl_3$	1:1	Extn. in presence of pyridine.	67
Acetylacetone dioxime								
Cu(II)	600		5.5	0.5–1 mg		1:1	Measured at 550 nm if Co and Ni are present. $\beta_1 = 8 \times 10^2$.	68, 69
Acetylacetone oxime								
Fe(II)	590		7.0	0.05–0.45 mg		1:2	Iron detd. in several drugs.	70
	590		7.5	2–30 μg	Butanol	1:2	Fe(III) red. to Fe(II) by $Na_2S_2O_3$; 96% extn.	71
Acetophenone oxime								
Fe(II)	650		7.8–8.5	2–30 μg	$CHCl_3$	1:2	99.3% extn., Fe(III) red. to Fe(II) by $Na_2S_2O_3$. Synthetic solutions and gun metal analysed.	71
Ni(II)	340	22.0	7.2–8.0	1–30 μg	$CHCl_3$	1:2	Ni detd. in cupronickel and stainless steels.	72
Pd(II)	420	10.3	0.1–1*N* acid	0.1–10 μg	C_6H_6	1:2		73
6-Acetyl-5-hydroxybenzo-1,4-dioxan oxime								
Ti(IV)	400		3.5–10.15	2.5–100 μg			6-propionyl, 6-butyryl derivatives also studied.	74
2-Acetyldibenzo-p-dioxan oxime								
Pd(II)	295	5.1		1–10 ppm	C_6H_6			75

Table 1—*Continued*

Ions	λ_{max}, nm	ϵ, 10^3 l.mole^{-1}.cm^{-1}	pH range	Range of detn.	Extraction	M:L	Remarks	Ref.
Biacetyl monoxime								
Pd(II)	320	4.8	4.0–5.0	0.9–9.5 μg	$CHCl_3$			76
Re(VII)	500	19.0	1*N* HCl	up to 20 ppm			In presence of $SnCl_2$ and HCl. 1000-fold Mo, Cu, W, V can be removed by extn. with quinoline.	77
Co(II)	336		8.75	0.4–14 × $10^{-5}M$			Interference by Al, Fe, Cu and Ni	78
Cu(II)			5.0–11.0		$CHCl_3$	1:2		79
Ni(II)			5.0–11.0		$CHCl_3$	1:2		79
Biacetyl monoxime semicarbazone								
Cu(II)	335	10.1	10.0	1–5.8 ppm		1:1	Comparative study between these complexes and the corresponding picolinaldehyde thiosemicarbazone is given.	80
Ni(II)	340	19.5	10.5–12.0	0.5–2.5 ppm		1:2		80
Co(II)	330	6.3	7.5–9.8	1–8 ppm		1:1		80
Pd(II)	390	2.9	4.0–10.0	3–29 ppm		1:2		80
Biacetyl monoxime thiosemicarbazone								
Co(II)	325	4.9	5.0	1–7 ppm		1:2	In presence of sodium citrate Ni(II) does not react, hence allows detn. of Co(II) in its presence.	81
Ni(II)	356	8.8	9.5			1:1		82
Fe(II)	335	11.5	5.3	1–4·5 ppm		1:2	Fe(III) is red. to Fe(II) by ligand, no prev. redn. is necessary.	83
	410	5.7	5.3	1–8.0 ppm		1:2		83
Cu(II)	345	10.6	8.5–9.5	0.5–5 ppm		1:1	Reaction is more sensitive in alkaline med.	84
Bi(III)	335		2.5–3.5	0–22 ppm	IBMK	1:2	Many cations interference.	84
Mn(III)	545	2.7	9.2–10.3					85
Biacetyl monoxime 4-phenyl-3-thiosemicarbazone								
Co(II)	345	17.7	3.8–8.0			1:2	$\beta_2 = 5.8 \times 10^{11}$	86
Ni(II)	375	17.1	5.2–10.0			Variable		86
Fe(II)	350	17.6	4.0–9.3			1:2	$\beta_2 = 1.4 \times 10^{10}$	86
Cu(II)	360	12.7	8.5–9.7			1:1		86
Mn(III)	550	3.6	10.0	2–12 ppm	Amyl alc.	1:2	$\beta_2 = 1.5 \times 10^{10}$	86

Biacetyl monoxime p-nitrophenylhydrazone								
Co(II)	520		Alkaline	0.25–5 ppm			Excess of reagent is extd. by ethyl ether. Interference of Fe, Cr, V, Mn removed by pptn. with aq. NH_3. Interference by large no. of cations reduced by addition of KCN.	87
Biacetyl monoxime 2-benzothiazolylhydrazone								
Pd(II)	560	5.1	Mildly acidic	10–150 μg	$CHCl_3$	1:2	Ir, Rh, Ru and Pt(II) tolerated up to 1000 ppm.	88
Benzamidoxime								
Co(II)	575		>13.5	up to 24 ppm			Mg, Mn, Fe(III), CN, SCN and EDTA interfere.	89
Benzimidazole-2-carboxanilide oxime								
Cu(II)	337	14.5	6.8–8.0		$CHCl_3$	1:1	Cu detd. in piston rod material	90
	340	10.6	3.9–5.0		$CHCl_3$	1:1		90
Co(II)	343	23.0	9.2–12.2		$CHCl_3$	1:2	Co detd. in cadmium.	90
	325	17.0	6.5–11.0		$CHCl_3$	1:2		90
Benzil α-dioxime								
Ni(II)	275	12.0	8.0–11.4	up to 20 μg	$CHCl_3$		With 5 μg of Ni, up to 10 μg of Co and 100 μg of Cu tolerated.	91
Fe(II)	559	0.37	9.0	<20 μg	$CHCl_3$		In presence of 4-picoline; interfering cations removed by ion-exchange.	92
Benzil α-monoxime								
Co(II)	380		8.75	$0.2–5 \times 10^{-5} M$			In presence of acetone Ni does not interfere.	78
Pd(II)	435		2.0–10.0	2–60 μg	$CHCl_3$	1:2	Sn(II), SCN^-, $S_2O_3^{2-}$ and EDTA interfere.	93
	435	12.5	4.0–5.0	up to 40 ppm	$CHCl_3$		Heating at 20°.	94
Ir(III)	405	13.0	4.0–5.0	up to 800 ppm	$CHCl_3$		Heating at 95° for 1 hr.	94
Rh(III)	435	1.2	4.0–5.0	up to 500 ppm	$CHCl_3$		Heating at 95° for 10 min.	94
	400		4.0–5.0	1–12 μg	$CHCl_3$		Pt(IV), Ru and Os interfere.	95
Pt(IV)	440	6.7	1.0–7.0	up to 22 ppm	$CHCl_3$		Heating on water-bath for 90 min.	96
α-Benzoinoxime (Cupron)								
Cu(II)	440		11.3–12.3		$CHCl_3$		Up to 1% of Cu detd. in Mo metal, molybdenite concentrates *etc.*	97
V(V)	550		2.2		$CHCl_3$		V detd. in steels.	98
Pd(II)	390		3.0		$CHCl_3$			99
Pt(IV)	450		3.0		$CHCl_3$		Aq. phase after extn. of Pd complex is heated for 30 min to form Pt(IV) complex.	99
Rh(III)	390	2.9	6.0	5–35 μg	$CHCl_3$		40 min heating, 8000-fold Pd(II) and 200-fold Pt(IV) tolerated.	100
Benzoylmethylglyoxime								
Pd(II)	280		3.6	10–60 μg	$CHCl_3$		1000-fold Pt(IV), Rh(III), Ir(III), Ru, Ni, Co or Cu do not interfere.	101

Table 1—*Continued*

Ions	λ_{max}, nm	ϵ, 10^3 l.mole^{-1}.cm^{-1}	pH range	Range of detn.	Extraction	M:L	Remarks	Ref.
5'-Chloro-2'-hydroxy-4'-methylacetophenone oxime								
Cu(II)	640		3.5	up to 0.95 μg	$CHCl_3$	1:2	Fe(III) interferes.	102
Ni(II)	580		8.0	up to 0.44 μg	$CHCl_3$	1:2		102
V(V)	400		2.5–4.0	5.1–30 ppm		1:2	75% ethanol, β_2 given for varied ethanol conc.	103
Cyclohexane-1,2-dione dioxime (Nioxime)								
Ni(II)	550	0.12	4.0–6.0	0.5–8 ppm			Gum arabic stabilizes the complex. Ni is detd. in calcium metal in presence of ammonium citrate.	104
	430	0.18	3.5	up to 7 ppm	Quinoline satd. with H_2O		Complex also extractable into C_6H_6. Method for sepn. of Ni from related cations given.	105
Re(VII)	440		≃0.6*M* HCl	20–50 ppm			Red. with $SnCl_2$, used to det. Re in refractory alloys.	106
Cyclohexane-1,2,3-trione trioxime								
Co(II)	400		3.0–4.0	1–4 ppm		1:3	Ni, Fe and Cu interfere at 100 ppm concn.	107
Ni(II)	430		3.0–6.0	5–25 ppm		1:2	Gelatin soln. used to stabilize the complex.	108
	560	2.2	3.0–6.0	1–25 ppm		1:2		108
Cycloheptane 1,2-dionedioxime (Heptoxime)								
Ni(II)	443	15.3	11.3	up to 15.4 ppm			In presence of Br_2 water.	109
	536	6.4	11.3	up to 15.4 ppm				109
	377	4.7	3.8–11.7	up to 10 ppm	$CHCl_3$		In absence of Br_2 water.	110
	377		4.0	up to 0.6 ppm	$CHCl_3$		Ni up to 0.6 μg can be detd. in 1-g sample of $CdCO_3$ or in zirconyl nitrate.	111
	377		2.7–12.4	1–5 μg	$CHCl_3$			112
Dimethylglyoxime								
Ni(II)	360	3.4	7.0		$CHCl_3$	1:2	Used to det. Ni in copper and its alloys and in cobalt.	142, 143
	262			0.5 μg	$CHCl_3$		Interferences masked with tartrate.	144
Pd(II)	366			11–63 μg	$CHCl_3$		Extn. into $CHCl_3$ allows sepn. from Au and Pt.	145
	295		<2*M* HCl	25–800 μg	$CHCl_3$		Ag, Au, Cu, Pd do not interfere.	146
Co(II)	435	10.6	6.0	2–20 μg			Reddish brown mixed complex of Co(II) dimethylglyoxime with iodide ion, modification to prevent interference by Cu, Hg, Pb also given.	141
Pd(II)	380	0.17	1.0–2.0	up to 12 ppm	$CHCl_3$		Detn. of 0.1–1.0% of Pd in titanium alloy.	147

Fe(II)	500		Ammoniacal	up to 50 ppm	$CHCl_3$	1:2	In presence of 2 moles of pyridine.	148
Re(VII)	445		Acidic	1–20 ppm	$CHCl_3$		In presence of $SnCl_2$ and tartric acid. Re detd. in alloys.	149
	445		~0.5*M* HCl	5–25 ppm			Red. with $SnCl_2$, Mo, W, Pt interfere. Re detd. in refractory alloys.	106
Dimethylpentane-2,3,4-trione trioxime								
Fe(II)	550		9.0–10.0	up to 2.5 μg			Sensitivity is better than 2,2′-bipyridyl or 2,2′,6,2″ terpyridyl.	150
2,4-Dimethylbenzamidoxime								
Co(II)	578		Alkaline	1.5–35 μg			50% ethanol, no interference from Cr(III), Fe(II), Mn(II), Ni(II), Cu(II) and oxidn. or redn. agents.	151
Dimedone dioxime								
Co(II)	400	23.0	9.0–9.5	up to 50 μg		1:1 & 1:6	Mole ratio method shows only 1:6 composition. Spot test for Co also given.	152
	370–380	11.3	Acidic	up to 50 μg	IBMK			152
Di-1-naphthyl diketone monoxime								
Co(II)	436		5.0–8.5	up to 2.7 μg	$CHCl_3$		Co detd. in metallic nickel.	153
Di(2-pyridyl) ketoxime								
Au(III)	459	20.0	2.0–3.5	1–10 ppm	Dichloro-methane	1:3	Extn. in presence of $KClO_4$.	154
	433		3.0	1.2–10 ppm			Au detd. in biological materials.	155
Co(III)	388	19.5	8.0–9.5	up to 3.5 ppm		1:3		156
Pd(II)	410	12.0	4.0–5.0	0.5–10 ppm	$CHCl_3$	1:2	CN^- must be absent.	157
Fe(II)	534	1.5	10.5–13.5	up to 4 ppm			Heating for 20–30 min, $NH_2OH.HCl$ used for redn. of Fe(III) to Fe(II). EDTA masks large no. of interfering ions.	158
	548	15.9	Highly alk. med.	0.89–2.53 ppm	Isoamyl alcohol		Fe detd. in KOH pellets, $Na_2S_2O_4$ used for redn. Heating for 20 min.	159
Di(2-pyridyl) α-glyoxime								
Pd(II)	404	10.1	2.5–4.0	1–14 ppm	$CHCl_3$		Only Sn^{2+}, Fe^{2+}, CN^- and oxidn. agents interfere.	160
Au(III)	448	17.0	1.5–8.0	1–11.5 ppm	75/25 ratio dichloro-methane/n-amyl alc.			161
Re(VII)	440	31.5	2*N* HCl	35–190 μg			Complex formed in presence of $SnCl_2$. If Mo is present, ReO_4^- must be extd. into pyridine.	162

Table 1—*Continued*

Ions	λ_{max}, nm	ϵ, 10^3 l.mole^{-1}.cm^{-1}	pH range	Range of detn.	Extraction	M:L	Remarks	Ref.
Fe(II)	488		4.5–7.8				Heating for 15 min at 60°, measured after 1 hr.	163
	486		4.5–7.8		Nitro-benzene		$NaClO_4$ present. Detn. of Fe *in situ* also discussed.	163
	534	13.3	10.5	15–300 μg			$NH_2OH.HCl$ and citrate soln. present, boiling for 5 min, large amount of Ni, Cu tolerated.	164
Di(2-pyridyl) β-glyoxime								
Fe(II)	558	19.0	5.8–9.8	0.5–3 ppm	$CHCl_3$		$NH_2OH.HCl$ present, pyridine–ethanol (2:1).	165
Di(2-quinolyl) ketoxime								
Co(II)	365	53.0	1–2*M* KOH	0.1–1.2 ppm	C_6H_6			166
Pd(II)	478	13.0	6.0–13.5	0.5–10 ppm	C_6H_6		Extn. in presence of EDTA.	167
2,5-Diacetylpyridine dioxime								
Fe(II)	490		12.5	0.1–5 ppm			$NH_2OH.HCl$ used for redn. of Fe(III) to Fe(II).	168
Cu(II)	360		12.5	0.1–5 ppm				168
Dibenzo-p-dioxan-2-aldoxime								
Pd(II)	318	17.0		0.2–6 ppm	C_6H_6		Effect of various conc. of HNO_3, ethanol and $Hg(NO_3)_2$ studied.	75
3',5'-Dichloro-2'-hydroxy acetophenone oxime								
Co(II)	400	1.4	7.0–8.0	1.7–10.3 ppm	$CHCl_3$	1:2	$\beta_2 = 5.2 \times 10^8$.	169
	420	1.3	7.0–8.0	1.7–10.3 ppm	$CHCl_3$	1:2	$\beta_2 = 5.3 \times 10^8$.	169
V(V)	400		2.5–4.0	5.1–35.7 ppm		1:2	75% ethanol, β_2 for varied ethanol conc.	103
MO(VI)	400	0.51	2.5–3.5	2–18 ppm		1:2	$\log \beta_2 = 7.28$	170
U(VI)	400	0.73	6.0–8.5	17–90 ppm		1:2	$\log \beta_2 = 6.39$	170
2,4-Dihydroxypropiophenone oxime								
Fe(III)	510	2.3	2.6–2.8	1–40 ppm		1:1	β_2 detd.	171
2,4-Dihydroxybutyrophenone oxime								
Fe(III)	510		2.7	1–56 ppm			Ionic strength 0.1*M* ($NaClO_4$).	172

2,4-Dihydroxyvalerophenone oxime								
Fe(III)	510		2.6–2.8	1–56 ppm		1:1	Parameters of Fe(III) complexes with oximes of corresponding acetophenone, propiophenone and butyrophenone are tabulated.	173
Cu(II)	640	0.16	2.5–5.0	45–80 ppm	$CHCl_3$	1:2	$\beta_2 = 3.7 \times 10^8$.	174
Ni(II)	580	0.16	7.0–9.0	38–70 ppm	$CHCl_3$	1:2	$\beta_2 = 2.8 \times 10^7$.	174
Pd(II)	400	0.77	2.0–5.0	35–75 ppm	$CHCl_3$	1:2	$\beta_2 = 6.4 \times 10^7$.	175
N,N'-Ethylenedi(4-methoxy-1,2-benzoquinone-1-oxime-2-imine)								
Pd(II)	420		1.0–3.5	4–100 ppm	$CHCl_3$		Interferences masked with EDTA.	176
Formaldoxime								
Mn(II)	455	11.2		up to 3 ppm		1:6	Use of CN^- as masking agent and heating at 90° makes method specific.	189
Ce(IV)	400	3.2	0.05–0.1*M* NaOH	up to 2 ppm		1:6	Th and other rare earths do not interfere. Ce detd. in apatite concentrates.	190 191
Ni(II)	473	18.4	>12.0	up to 2 ppm		1:6		192
V(V)	403	6.6	6.0–7.0	up to 5 ppm		1:3	When ratio of V to CH_2NO^- is $\simeq$1:400, 1:6 complex is formed.	193
	410		Ammoniacal	0.7–33.0 μg			Modified procedure.	194
Fe(II)	534	7.4	Alk. med.	up to 5 ppm		1:3		190
Furil α-monoxime								
Co(II)	395–415		5.0–6.0	1–200 μg	$CHCl_3$		In presence of pyridine. Method used for detn. of Co in steel, tech. nickel and pyrrhotities.	195
Co(III)	405–410		2.5–7.0	0.5–25 μg	C_6H_6		Co detd. in tech. iron samples.	196
Furil α-dioxime								
Re(VII)	532	41.3	0.035*M* HCl	up to <100 μg			In presence of $SnCl_2$ and acetone only Mo, Cu, Pd interfere.	220
	530		~1*M* HCl	1–5 ppm	$CHCl_3$		Red. with $SnCl_2$, only Mo, Pt interfere, used to detn. Re in refractory alloys.	106
	532	41.3	0.035*M* HCl	up to <300 μg		1:2	Interference of Mo removed by extn. of Mo ethyl xanthate complex into $CHCl_3$.	221
	532		7.0	up to 60 ppm			Up to 500-fold Mo tolerated.	224
Cu(II)	445		9.5	0.25 mg	$CHCl_3$		Cu sepd. from Co and Ni by back-extn. with H_2SO_4, pH raised to 9.4 and extn. with $CHCl_3$. Tartrate masks Al, Fe, Ti. Used to analyse silicate rock and minerals.	203

Table 1—*Continued*

Ions	λ_{max}, nm	ϵ, 10^3 l.mole^{-1}.cm^{-1}	pH range	Range of detn.	Extraction	M:L	Remarks	Ref.
Pd(II)	297	2.0	3.0–4.0	Small amount	C_6H_6		Interference of Au removed by $NH_2OH.HCl$; only Fe(III) interferes.	222
	420		0.1–1.4*M* HCl	up to 3 ppm			10% ethanol necessary.	226
	380		0.1–1.4*M* HCl	up to 3 ppm	$CHCl_3$	1:2	Other Pt metals do not interfere.	226
Ni(II)	435	14.5	Slightly acidic	1–20 ppm	$CHCl_3$		In presence of $K_2Cr_2O_7$ and sodium citrate.	223
	435		~9.0	5–15 μg	$CHCl_3$		Cu, Co interfere, used to detn. Ni in silicates, sulphide, soil, rocks.	209
Fe(II)	570	8.9	2.4	5–25 ppm	$CHCl_3$		Synergic extn. in presence of 1*M* pyridine. Fe detd. in several alloys.	227
Co(II)	350		8.0	up to 4 ppm			Cu, Ni, Fe, Pb interfere.	225
Au(III)	330	31.6	1.8	9–45 ppm	$CHCl_3$		Extd. in $CHCl_3$ in presence of pyridine. Sepn. of Au from related metals given.	228
U(VI)	428	3.2	6.0–8.6	25–400 μg			No interference by Pb, Fe(III), Th or V(V).	229
Glutarimide dioxime								
Ce(III)	480		10.3–12.2	5–120 ppm			Method for detn. of Ce(III) in a mixture containing La, Nd, Fe.	230
Glyoxime								
Pd(II)	397	0.45	1.0	0.1–0.35 mg	$CHCl_3$	1:2	Interference can be masked with EDTA.	231
Co(II)	286	15.0	8.0–9.5	up to <4 ppm			Interference by Cu, Ni, Fe(III) and Al masked with EDTA.	232
O-Hydroxyacetophenone oxime								
Fe(III)	570	4.3	2.0–2.5	up to 0.1 mg		1:1	Interference by vanadate, $C_2O_4^{2-}$, F^-.	233
	420		3.7–8.5	up to 0.1 mg		1:2	Complex stable for 2 weeks.	233
V(V)	400	1.3	2.8–3.9	up to 7.2 mg			Cu, Ni, Pd interfere.	234
U(VI)	420		9.7–11.1	>120 ppm			Heavy metals, VO_3^-, PO_4^{3-} interfere.	235
O-Hydroxybutyrophenone oxime								
Fe(III)	510	1.0	2.9	1–56 ppm				236
2-Hydroxy-5-methoxybenzaldoxime								
Mo(VI)	370		3.2–3.8	5–70 ppm		1:1	Mo detd. in lubricating oil.	237
	400		3.2–3.8	5–110 ppm		1:1		237

2-Hydroxy-4-methoxy-5'-methylchalcone oxime								
Pd(II)	380	3.4	0.5–2.5	1–30 μg	Isobutanol	1:2	Pd sepd. from large no. of interfering cations.	238
	380		1.0	10–700 μg	Isobutanol		Sepn. of Pd(II) from Cu(II) possible.	239
Cu(II)	375		5.8	10–700 μg	C_6H_6			239
	340		4.0			1:1		240
	370	7.2	4.4–5.8	0.5–11 μg	$CHCl_3$	1:1 & 1:2	Two mixed species are obtained with λ_{max} at 340 and 370 nm.	240
2-Hydroxy-1-naphthaldoxime								
U(VI)	470		9.0–11.0	0.5–5 mg		1:2		241
2-Hydroxy-5-methylpropiophenone oxime								
Fe(III)	580	6.2	2.05–2.15	up to 28 ppm		1:1	75% ethanol.	242
	500	2.3	8.5–9.5	up to 45 ppm		1:3	20% ethanol.	242
Ni(II)	590	0.15	0.1–1.0*M* NH_3		$CHCl_3$	1:2		243
Pd(II)	375	4.9	1.0–4.0	up to 15 ppm	CCl_4	1:2	$\beta_2 = 2 \times 10^9$.	244
8-Hydroxy-5-methoxytetralone oxime								
Cu(II)	400		6.0–7.0	up to 50 ppm	$CHCl_3$			245
4-Imino-1,3-dimethylalloxan-5-oxime								
Cu(II)	382	5.1	8.0	1–13 ppm		1:1	Only Co, Pd, Ni and Fe(II) interfere.	246
2-Isatoxime methyl ether								
Cu(II)	539		5.0–7.0	1–20 ppm	$CHCl_3$		In presence of NaK tartrate; *interference only by Hg(+ KI).*	249
4-Isopropylcyclohexane-1,2-dione dioxime								
Ni(II)	383		7.0	0.5–10 ppm	Xylene		0.005–100 ppm of Ni detd. in water, alkali metals and several analytical reagents.	250
4-Methylcyclohexane-1,2-dione dioxime								
Ni(II)	365	3.3	5.0–5.5	up to 8 ppm	Toluene			251
	365	3.3	5.0–5.5	up to 2 ppm	Toluene		Tartaric acid used when Th, Fe, Cr present; thioglycollic acid when U, Cu, Fe and Cr present.	251
Pd(II)	280	1.5	0.7–5.0	up to 10 ppm	$CHCl_3$		Cu masked with thioglycollic acid. Co^{2+} converted into hexacyanocobaltate and Fe oxidized to Fe^{3+} which is masked with F^-.	252
Re(IV)	436	68.9	7.0	up to ≯160 μg	$CHCl_3$		Method applicable to detn. of 0.001–1% Re in molybdenite concentrate and molybdenite roaster flue dust.	253

Table 1—*Continued*

Ions	λ_{max}, nm	ϵ, 10^3 l.mole^{-1}.cm^{-1}	pH range	Range of detn.	Extraction	M:L	Remarks	Ref.
Methyl-2-(4-ethylpyridyl) ketoxime								
Fe(II)	568	23.4	4*M* NaOH		Isopentyl alc.		Reagent superior to 1,10-phenanthroline for detn. Fe(II) in alk. soln.	254
Cu(I)	430	9.7	4.0–5.0					254
Co(II)	338	16.5	4.0–11.0					254
3-Methylglyoxime								
Co(II)	260		8.0–9.5	up to 7 ppm			Interference of Ni masked with EDTA.	255
6-Methylpicolinamide oxime								
Cu(I)	405	7.2	4.5–7.0	up to 0.1m*M*	Isopentyl alc.		Cu detn. in blood and liver.	256
6-Methylpiconaldoxime								
Fe(II)	520		7.3–10.0	1.12–28 ppm			50% acetone medium, 10–45°.	257
Methyl-2-pyridyl ketoxime								
Re(VII)	490	3.8	Acidic	10–50 ppm		1:1	In presence of $SnCl_2$. Several interferences prevented by measuring at 630 nm.	258
Cu(I)	410	6.4	10.0–11.7	0.5–37 ppm		1:2	Cu(II) gives same reaction, as reagent reduces Cu(II) to Cu(I).	259
Fe(II)	525	14.0	10.5–6*N* alk.	0.05–10 ppm		1:3	Simultaneous detn. of Cu(I) is possible.	259
6-Methyl-2-pyridyl phenyl ketoxime								
Cu(I)	460	11.0	12.0		Isoamyl alc.	1:2	Cu detd. in alk. med.	260
	430	10.8	3.5–6.5			1:3	Two complexes formed, at different pH-values.	260
p-*Methoxyphenylpyruvic acid oxime*								
Cu(I)	580		Alk. med.	3–100 ppm		1:2	Another complex with 1:1 composition is formed with λ_{max} 640 nm.	261
1-Naphthamidoxime								
Co(II)	581	4.4	weakly alk.	0.5–9 ppm	Isobutyl alc.		β detd.	262
1,2-Nathpthaquinone dioxime								
Ni(II)	468	21.9	5.0		$CHCl_3$	1:3	Extd. in presence of zephiramine. Effect of $-SO_3H$ group in various positions compared. $-SO_3H$ group in 6-position is most sensitive.	263
Nicotinamidoxime								
U(VI)		5.3	10.9–11.5	5–40 ppm			Several interferences removed by tartrate and EDTA.	264
Co(II)	540	5.9	10.5–11.0	2–16 ppm			Most anions and cations interfere.	265
Ni(II)	575	4.2	≃11.0	0.3–10 ppm			Ni sepd. from Cu, Co, Zn, Mn, Fe^{3+} by anion-exchange.	266

Oxamidoxime								
Co(II)	350	8.6	8.0–9.5	1–50 ppm				267
Ni(II)	233	21.0	3.0–5.0	1–30 ppm		1:2	Ni pptd. at pH 8–9.5. Ppt soluble in dil. mineral acids, DMF and strongly alkaline med.	267
n-Pentyl-2-pyridyl ketoxime								
Cu(I)	360	2.7	2.5–3.0	up to $5.6 \times 10^{-4} M$	Isoamyl alc.			268
Phenanthrenequinone monoxime								
Co(II)	470	17.5	4.4–8.0	up to 3 ppm		1:3	Heating on water-bath for 3 min.	269
Pd(II)	430	15.0	2.5–5.0	up to 3.3 ppm		1:2	$\beta_2 = 7 \times 10^{11}$. Ni, Cu, Co masked with F^-.	270
	500	13.3	2.5–5.0	up to 3.4 ppm		1:2	$\beta_2 = 6 \times 10^{11}$.	
Fe(II)	640	13.8	4.2–6.0	up to 0.84 ppm	$CHCl_3$	1:3	$NH_2OH.HCl$ used to prevent aerial oxidation.	270
Ru(III)	550	11.0	4.2–5.4	up to 4.4 ppm	$CHCl_3$	1:2	150 min heating, Ru detd. in presence of U(VI).	270
	660	12.5	4.2–5.4	up to 4.0 ppm	$CHCl_3$	1:2		270
Rh(III)	400	12.5	4.9–6.7	up to 4.2 ppm		1:3	3 hr heating.	270
	500	12.3	4.9–6.7	0.2–4.2 ppm		1:3		270
Phenoxatiin-2-aldoxime								
Pd(II)	380		0.5*M* HNO_3	0.25–8 μg	C_6H_6	1:4	In presence of 3% $Hg(NO_3)_2$ to mask Cl^-.	271
Phenylazobenzaldoxime								
Co(II)	530		7.0–8.0	0.6–3.5 ppm			Analogous 4-methoxy, 2- and 4-chloro- and 2,2- and 4-nitrophenyl azo-compounds can also be used.	272
Phenyl α-(4-ethylpyridyl) ketoxime								
Fe(II)	566	25.7	4*M* NaOH		Isopentyl alc.		Reagent is superior to 1,10-phenanthroline for detn. of Fe(II) in alk. soln.	254
Phenyl α-pyridyl ketoxime								
Au(III)	450		3.0–6.0	0.4–8 ppm	$CHCl_3$		Interference by Cu, Co and Ni masked with EDTA, ppte. of Ag, Bi and Fe(III) removed by filtration.	273
Pd(II)	340	50.0	8.5–10.0	1.5–8 ppm	$CHCl_3$	1:2	EDTA masks common interfering cations.	274
	410	30.0	8.5–10.0	2.0–8 ppm	$CHCl_3$	1:2		274
Fe(II)	550	15.6	9.0–11.0	$> 10^{-4} M$	Isoamyl alc.	1:3	Fe detd. in alkalis, sand and Na_2CO_3 solutions.	275
	550	15.0	Highly alk.	up to 2.8 ppm			Iron detd. in glass sand.	276
	588	15.2	>12.0	up to 8 ppm	Isoamyl alc. + ethanol	1:2	Fe detd. in ethylenediamines.	277
	570	11.6	Alk.	0.05–1 ppm	$CHCl_3$		Fe detd. in ground water; ascorbic acid for reduction.	278

Table 1—*Continued*

Ions	λ_{max}, nm	ϵ, 10^3 l.mole^{-1}.cm^{-1}	pH range	Range of detn.	Extraction	M:L	Remarks	Ref.
Pb(II)	340			1.5–8 μg			Au(III), CN^- interfere.	279
Re(VII)	510	7.3	Mildly acidic	0.02–0.4 mg		1:1	In presence of $SnCl_2$.	280
Au(III)	455	9.4	9.0	up to 80 μg	$CHCl_3$		Simultaneous detn. with Pd(II).	281
Pd(II)	410	9.2	9.0	up to 50 μg	$CHCl_3$		Analysis of binary alloy and plating bath.	
Fe(II)	550	11.9	10.0	up to 0.04 mg	$CHCl_3$		Simultaneous detn. with Cu(II).	282
Cu(II)	475	3.9	10.0	up to 0.2 mg	$CHCl_3$		Synthetic solutions and ferrite analysed.	
Pd(II)	410	9.8	10.0	up to 11 ppm	$CHCl_3$		Simultaneous detn. with Au(III)	283
Au(III)	455	9.4	10.0	up to 8 ppm	$CHCl_3$		and Cu(II) possible. Method	
Cu(II)	550	2.5	10.0	up to 6 ppm	$CHCl_3$		applied to ternary alloys.	
Phthalimide dioxime								
Pd(II)	430		4.6	5 μg–2 mg		3:2	Reagent prepared in 2-ethoxyethanol.	284
Picolinaldoxime								
Pd(II)	322	10.3	3.5–11.5	1.88–11.3 ppm	$CHCl_3$	1:2	Large number of interferences	285
	404	10.4	3.5–11.5	1.88–11.3 ppm	$CHCl_3$	1:2	masked with EDTA. Synthetic solutions analysed.	
Au(III)	420		2.0–4.0	0.3–13 μg		1:2		286
Co(II)	380		>4.0	≃10 μg			Higher conc. can be measured at 400 or 420 nm.	286
Ru(III)	420	2.3	1.6–11.3	3–3.5 ppm		1:2		287
Fe(II)	510		5.5–7.4	0.52–12.9 ppm				288
	520		Above 10.0	0.26–7.74 ppm				288
			10.0–13.0	0.5–5 ppm			Complex is unaffected by reducing agents used for Fe^{3+}.	289
Cu(II)	422		4.5–6.5	0.1–10 μg			$NH_2OH.HCl$ present.	290
	445		>12.0	0.1–10 μg			$NH_2OH.HCl$ present.	290
	420		4.0	2–50 μg	Butanol		Soln. of Cu is treated at pH 8.5 with reagent and extd. with butanol. Ext. is dried and treated with ascorbic acid and phthalate buffer of pH 4. Ni is not extd., Fe is masked with NH_4NaHPO_4.	291
Pyridil α-monoxime								
Pd(II)	416		1.0	1–13 ppm	$CHCl_3$		CN^- must be absent.	292
Co(II)	408	17.0	4.5–7.0	0.4–4 ppm	$CHCl_3$	1:3	Structure for cobalt chelate based on analysis and infrared evidence given.	293

Pyridine-2,6-diacetaldoxime								
Mn(III)	598		9.5–11.5	0.1–11.5 μg			Green complex formed on warming soln. Reducing agents must be absent. At high metal concn. red complex is formed.	294
Pyridine-2,6-diamidoxime								
Fe(II)	523	16.8	0.01–5*M* NaOH	0.4–7 ppm		1:2	Fe detd. in alkali metal hydroxides, Fe reduced by sodium dithionate.	295
2-Pyridyl-2-thienyl-β-ketoxime								
Co(II)	412	20.0	7.0–10.8	0.15–2.7 ppm	$CHCl_3$		40% sodium citrate present.	296
Quinoline-2-aldoxime								
Pd(II)	365		>5.0	up to 70 μg	$CHCl_3$		Cu and Pt masked with EDTA. No other Pt metals interfere.	297
Cu(I)	467		4.5–8.5	up to 10 μg			Redn. of Cu(II) with $NH_2OH.HCl$. Pd and other coloured cations interfere.	298
5,8-Quinolene dione dioxime								
Co(II)	416	14.8	6.3–7.6	0.08–7 μg	Isoamyl alc.		No interference by 1000-fold Fe	299
Quinisatin oxime								
Fe(II)	660	16.2	5.0	0.5–2.4 ppm		1:3	Reaction conducted in DMF. Reagent redn. Fe(III) to Fe(II) but 1% quinol used for complete redn.	300
Os(VIII)	515	15.5	5.0	3–10 ppm		1:2	Heating for 1.5 hr below b.p.	301
Resacetophenone oxime								
Fe(III)	580		6.3–8.3	1–14 ppm			10% ethanol.	302
Ni(II)	595	0.13	8.0–11.0	6–1500 ppm	Cyclo-hexanone	1:2	Ni can be back extd. into aq. phase at pH <4.	303
U(VI)	420		5.6	0.3–5 mg			Fe interferes, but Al, Zr, Th do not.	304
Salicylamidoxime								
U(VI)	400		7.9–9.1	7–145 ppm			Most cations interfere.	305
Fe(III)	400		8.3–10.0				Most cations interfere.	306
Salicylaldoxime								
Cu(II)	344		3.5–9.5	1.6–5.5 ppm	n-amyl alc.		Cu detd. in aluminium alloys.	307
Fe(III)	480	5.1	6.2–6.6	0.1–2.2 ppm				308
Mo(VI)	400	0.69	3.2–3.7	up to 100 ppm				309
Ni(II)	387		8.5–9.4	up to 100 μg	$CHCl_3$		First Ni detd. by extn. and then Cu detd. similarly.	310
Cu(II)	345		3.0–8.0	up to 80 μg	$CHCl_3$			310

Table 1—*Continued*

Ions	λ_{max}, nm	ϵ, 10^3 l. mole^{-1} . cm^{-1}	pH range	Range of detn.	Extraction	M:L	Remarks	Ref.
4-Tert. butylcyclohexane-1,2-dione dioxime								
Ni(II)	386	4.1	7.0	0.85–17 ppm	Xylene		Ni detd. in Sc, Y and rare earth samples.	311
p-Toluamidoxime								
Co(II)	580		Alkaline	25–200 μg				312
	580		Alkaline	10–80 μg	Butanol, isobutanol or heptanol			312

They are applied for trace determination of metal ions in various materials.

Dimethylglyoxime, a well known reagent for nickel, has been applied for its determination in steels, aluminium alloys[113,114] uranium and its compounds,[115–117] petroleum cracking catalysts,[118] soils,[119] copper ores and alloys,[120,121] iron ores,[122] niobium, molybdenum, tungsten and its alloys,[123–125] zinc and cadmium,[126] lead and antimony,[127] zirconium,[128] sea-water[129,130] foodstuffs,[131–134] air[135] and cement.[136] Dimethylglyoxime has also been used to determine iron in copper alloys[137,138] and rhenium in molybdenum and tungsten ores and flue dust.[139] Dimethylglyoxime (dmg) mixed complexes are useful in selective analytical procedures. For example, the red colour of the mixed complex of iron(II) with dmg and ammonia allows the selective spectrophotometric determination of iron(II).[140] The cobalt(II)–dmg–iodide mixed complex is suitable for the specific determination of cobalt on the micro scale.[141]

Formaldoxime has been used in spectrophotometric determination of manganese in natural water,[177] plant material,[178] biomaterials,[179] nickel alloys,[180] silicate and carbonate minerals,[181] ores and rocks,[182] soil,[183] tin[184] and animal feed.[185] The method has also been automated for the determination of manganese in water[186] and in silicate minerals.[187] It is also used for determination of iron in water.[188]

Furil α-dioxime is used for spectrophotometric determination of rhenium in ores and in presence of large amounts of molybdenum,[197–199] in tantalum–rhenium alloy,[200] plutonium–rhenium alloy[201] and minerals,[202] and for copper in rocks and minerals,[203] palladium in fine gold[204] and indirect determination of cyanide[205–207] and perchlorate.[208] It has also been used for spectrophotometric determination of nickel in steels, silicate and sulphide minerals,[209] petroleum oil,[210] boiler feed-water,[211] alkalis,[212,213] rhenium,[214] cadmium,[215] indium and aluminium,[216] silver,[217] tin,[186] beryllium[218] and various other metals.[219]

Heptoxime[247] is used to determine nickel in silicate minerals, Ge, Zr and Cd salts, In and Ga metals.

Nioxime and furil α-dioxime have been proposed as reagents for spectrophotometric analysis of Ni–Fe, Ni–Re and Cu–Fe mixtures.[248]

The reaction between rhenium and α-furil dioxime has been applied to an indirect spectrophotometric determination of 3–5 ppm of nitrate.[313] Perrhenate and nitrate form a complex that is not reducible with stannous chloride in acid medium.

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DOSAGE COULOMETRIQUE PRECIS DES ACTINOIDES; APPLICATION A DE FAIBLES MASSES—II

AMERICIUM

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Résumé—Une méthode de détermination de l'américium par dosage coulométrique à intensité imposée est proposée. Le dosage est basé sur la réduction à une électrode de mercure des ions mercuriques déplacés de leur complexe avec l'acide éthylenediaminetétracétique par l'américium. La détermination du point équivalent est faite par ampérométrie à deux électrodes polarisées. On décrit la cellule de mercure et l'appareillage qui permet dans les conditions optimum d'obtenir des précisions de l'ordre de 0,1% sur des prises d'essai de 700 μg d'américium et de 0,2% pour 300 μg (σ mt à 95% de confiance). Les mesures effectuées sont des mesures absolues ne nécessitant pas d'étalonnage préalable. Le temps nécessaire à une détermination est de l'ordre de une heure. Les résultats des comparaisons effectuées avec d'autres méthodes de mesures sont donnés ainsi qu'une étude sommaire des éléments gênants.

Parmi les méthodes de dosage récemment proposées pour la détermination de l'américium, le dosage complexométrique à l'acide éthylènediaminetétracétique (EDTA) est celui qui semble donner les meilleurs résultats. Successivement Yamamura,[1] MacCracken *et al.*,[2] Timofeev *et al.*,[3] enfin Buijs et Bartscher[4] ont proposé des méthodes basées sur l'emploi d'une solution étalonnée de complexant comme titrant, la fin de réaction étant déterminée à l'aide d'un indicateur coloré ou par potentiométrie. Ces méthodes rapides et précises ne donnent malheureusement pas une mesure absolue.

Les seuls dosages absolus de l'américium sont les dosages par coulométrie à potentiel imposé proposés par Koehly[5] puis Stokely et Shults.[6] La difficulté d'obtenir, puis de stabiliser la valence VI de l'américium, rend aléatoire l'utilisation en routine de ces méthodes de dosage.

Pour obtenir des mesures absolues, tout en gardant les avantages du dosage complexométrique à l'EDTA, nous avons, dans cette étude, appliqué au dosage de l'américium la technique du titrage coulométrique à courant constant de Reilley et Porterfield,[7] technique adaptée par la suite aux dosages de petites quantités de terres rares par Monk et Steed[8] et MacCraken *et al.*[9]

La méthode est basée sur la réduction électrochimique des ions Hg^{2+} déplacés du complexe Na_2Hg EDTA par l'ajout d'américium suivant l'équilibre:

$$Hg\,EDTA^{2-} + Am^{3+} \rightleftharpoons Am\,EDTA^{-} + Hg^{2+}$$

Les ions Hg^{2+} libérés sont réduits à une électrode de mercure. Le courant de réduction intégré est directement proportionnel à la quantité d'américium ajoutée dans la cellule de mercure. La détermination du point équivalent est faite par potentiométrie ou par ampérométrie.

PARTIE EXPERIMENTALE

Appareillage

Boîtes à gants. En raison de la radioactivité élevée des isotopes de l'américium, toutes les manipulations ont été effectuées en boîtes à gants. La chaîne de mesure comprenait une boîte contenant une balance de précision et une boîte où était placé le stand de mesure.

Cellule de mercure. Nous avons adapté pour les dosages d'américium une cellule de mesure conçue pour la coulométrie à potentiel contrôlé de l'uranium et précédemment décrite.[10] Cette cellule représentée sur la figure 1 est en "Plexiglas" poli; son diamètre intérieur est de 33,5 mm; elle est pourvue à sa base d'un fil de platine assurant la liaison électrique avec la nappe de mercure. Le volume minimum d'électrolyte nécessaire est de 3 ml. L'agitation est assurée par un agitateur en "Lucoflex" de forme étudiée; son diamètre est de 16 mm et sa vitesse de rotation 3000 t/mn. La désaération est effectuée en admettant au dessus de la solution une surpression d'azote, surpression réglable à l'aide d'un manomètre. Le compartiment auxiliaire est un tube de verre "Pyrex" obturé par un fritté No 4. L'électrode auxiliaire est un fil de platine.

Electrodes indicatrices. Deux types d'électrodes indicatrices ont été employées: microélectrodes de Pt amalgamé et microélectrodes d'or amalgamé. L'ensemble le plus fiable est celui représenté par la figure 2. Deux fils d'or de diamètre 1,7 mm sont noyés dans un embout en "Teflon" monté à force sur un tube en "Téflon". L'extrémité des fils d'or est polie avec soin, dégraissée puis amalgamée par dépôt électrolytique de mercure.

En fonctionnement normal, chaque matin les microélectrodes subissent un traitement d'activation: traitement anodique à 500 μA pendant 200 sec, l'électrolyte étant la solution de complexe Hg $EDTA^{2-}$, puis traitement cathodique à 200 μA pendant 900 sec.

Quand malgré le traitement d'activation, la réponse des électrodes devient moins rapide ou plus erratique, on nettoie les électrodes par trempage dans l'acide nitrique (10*M*) puis par une abrasion avec du papier très fin on renouvelle la surface des électrodes qui est à nouveau amalgamée. Cette opération peut être renouvelée jusqu'à ce que l'embout soit completement usé.

Ensemble de mesure. Tous les dosages ont été effectués avec un ensemble Tacussel comprenant un générateur cou-

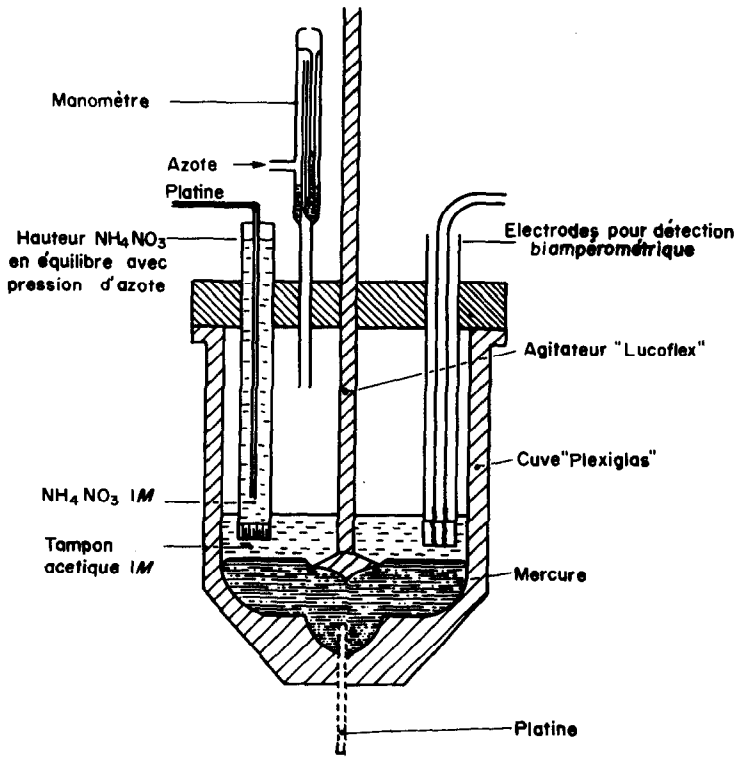

Fig. 1. Cellule de coulométrie.

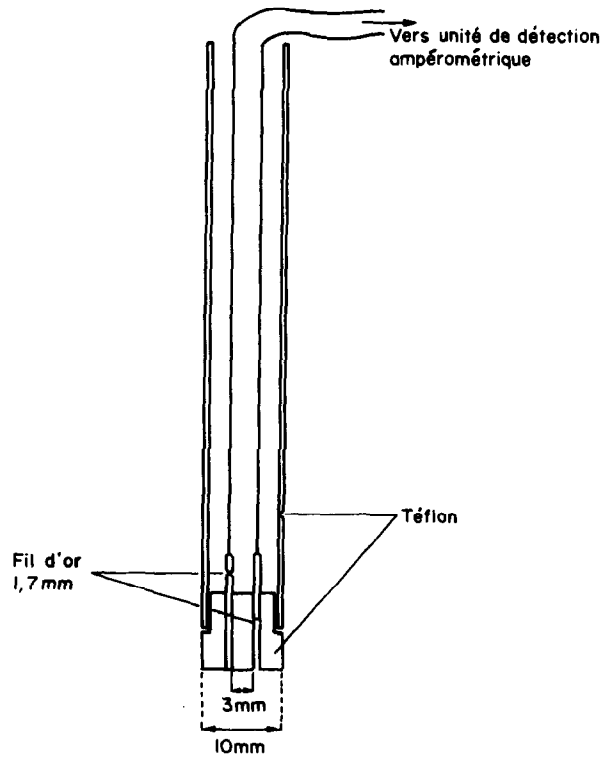

Fig. 2. Electrodes pour détection ampérométrique.

lométrique type GCU, une unité de détection potentio-ampérométrique type UDPA et une unité d'intégration de courant type UAIC. Cet ensemble permet la génération d'un courant constant et l'intégration de ce courant. L'unité de détection potentiométrique ou ampérométrique peut piloter le générateur de courant (arrêt de la génération à un point prédéterminé par exemple). Le tracé des courbes ampéropotentiométriques est effectué à l'aide d'un enregistreur Tacussel type EPL2.

Réactifs

Solution de complexe Hg EDTA^{2-}. Pour un litre de solution complexante, 2,20 g de mercure sont dissous dans l'acide nitrique, on ajoute à la solution 3,72 g de Na_2 EDTA, 57 ml d'acide acétique glacial et la quantité nécessaire d'ammonia que pour amener le mélange à pH 5. La solution est conservée en flacon polythène. Tous les produits utilisés sont des produits pour analyse.

Solution d'américium et de terres rares. Les solutions de terres rares ont été obtenues par dissolution de l'oxyde de haute pureté et diluées par pesée. Les solutions de ^{241}Am et de ^{243}Am ont été préparées à partir de l'oxyde. Les solutions obtenues ont été purifiées par chromatographie en phase inverse sur colonne D_2EHPA/Gaz Chrom Q, selon un mode opératoire précédemment décrit.[11] Les solutions purifiées sont précipitées par l'acide oxalique, l'oxalate obtenu étant ensuite transformé en oxyde par chauffage. L'oxyde obtenu est dissous dans l'acide nitrique puis dilué au poids desiré.

Mode opératoire

On introduit dans la cellule de mesure 7 ml de mercure puis 3 à 9 ml de solution de complexe Hg EDTA^{2-}. Le compartiment auxiliaire est rempli d'une solution de nitrate d'ammonium 1*M*, la cellule est placée sur son support et on effectue sous agitation une désaération de 10 mn environ.

Le seuil de l'unité de détection ampèrométrique est fixé à 0,5 μA et le potentiel appliqué entre les deux microélectrodes d'or amalgamé à 20 mV. On procède alors en mode automatique à la réduction des ions Hg^{2+} libres présents dans la solution de complexe Hg EDTA^{2-}. Le courant de réduction est fixé à 500 μA. Lorsque le courant passant dans le circuit de détection atteint la valeur de 0,5 μA fixée comme seuil, le circuit est coupé automatiquement. On passe alors en mode manuel, la valeur du courant est fixée à 200 μA et la réduction est poursuivie en enregistrant la courbe ampérométrique et en intégrant le courant. Quand l'enregistrement de la courbe permet de déterminer avec précision le point équivalent, on coupe le circuit et on détermine graphiquement le quantité de courant ayant passé dans le circuit après le point équivalent (soit n_1 cette quantité).

On ajoute alors dans la cellule de mesure une aliquote pesée de la solution à doser et on dégaze pendant 5 mn.

La réduction des ions Hg^{2+} libérés s'effectue alors en mode automatique à 500 μA (soit N le nombre de coulombs correspondant à cette partie du dosage) puis en mode manuel comme décrit ci-dessus soit n_2 la quantité d'électricité consommée pour atteindre en mode manuel le point équivalent.

La quantité d'électricité totale est donc $n_1 + N + n_2 = Q$ coulombs. Si P = poids de l'aliquote de la solution à doser; M = masse atomique de l'américium; C = concentration de la solution d'américium; F = le faraday (96485C), on a $C = QM/2PF$.

RESULTATS ET DISCUSSION

Choix du milieu tampon et du pH

Les constantes de stabilité des complexes Am EDTA$^-$ et Hg EDTA^{2-} sont respectivement de $10^{18.06}$ et de $10^{22.1}$.[12] Pour obtenir un dosage complexométrique précis, il faut d'après Ringbom:[13]

1. que les constantes de stabilité conditionnelles des deux chélates soient supérieures à 10^7;

2. que la constante de stabilité conditionnelle du chélate Am EDTA$^-$ soit beaucoup plus grande que celle du chélate Hg EDTA^{2-}.

D'après Monk et Steed[8] et McCracken *et al.*[9] ces conditions sont satisfaites pour certaines terres rares (Nd, Ce, Y,...) dans les milieux tampon acétique en opérant à un pH supérieur à 4. Vu les difficultés, faute de données, de calculer les constantes conditionelles des complexes Am EDTA$^-$ et les similitudes des propriétés chimiques entre l'américium et les terres rares, nous avons étudié expérimentalement les milieux acide acétique–acétate d'ammonium et acide acétique–acétate de sodium. Ces deux milieux tampons donnent de bons résultats mais nous avons préféré le milieu acide acétique–acétate d'ammonium qui donne les meilleurs virages en ampérométrie à deux électrodes polarisées.

Des essais effectués avec le néodyme puis avec de l'américium nous ont amenés à opérer à pH 5. A un pH inférieur à 4, le dosage n'est plus quantitatif, d'autre part, si on fixe le pH à une valeur supérieure à 6, on risque une hydrolyse de l'américium et surtout de doser d'éventuelles impuretés (alcalino terreux).

Choix de la méthode de détection

Parmi les méthodes de détection du point équivalent envisageable, nous avons expérimenté la potentiométrie à courant nul, la potentiométrie à courant imposé et l'ampérométrie à deux électrodes polarisées (dead-stop end-point).

La potentiométrie à courant nul a été rapidement abondonnée, le saut de potentiel obtenu étant à pH 5 trop faible (de l'ordre de 50 mV) pour obtenir une indication précise du point équivalent.

Comme Monk et Steed[8] l'avaient constaté dans des conditions de mesure semblables, les courbes de titrages (Fig. 3-a) obtenues en potentiométrie à courant imposé ne permettent pas un repérage aisé du point équivalent. Nous avons donc choisi comme "point équivalent apparent" un potentiel fixé arbitrairement avant le maximum, pendant la montée rapide du potentiel. En opérant selon le processus illustré par la figure 3-b, avec un potentiel de consigne, nous obtenons un dosage automatique qui sera juste si la pente et la hauteur des vagues de prétitrage (préréduction) et de titrage (réduction) sont similaires. Les mesures ont été effectuées sur deux microélectrodes d'or ou de platine amalgamé.

La reproductibilité obtenue est bonne: des erreurs relatives moyennes (σ) de 0,1% à 95% de confiance ont été obtenues sur le titre d'une solution de zinc. Malheureusement, nous n'avons jamais pu obtenir des microélectrodes donnant des réponses stables dans le temps. Au bout de quelques heures, la hauteur du saut de potentiel commençait à varier, ce qui

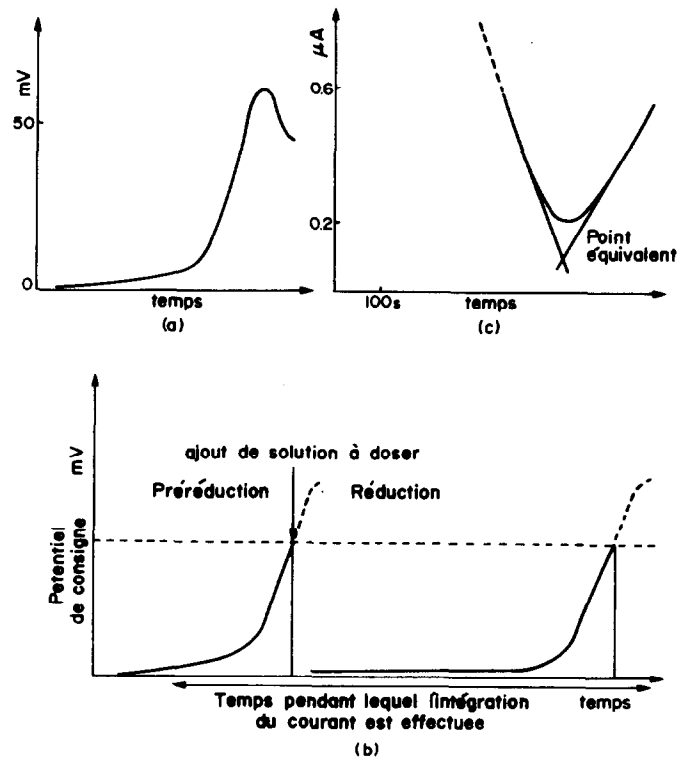

Fig. 3. (a) Courbe de virage en potentiométrie à courant imposé; (b) détection par potentiométrie à courant imposé; (c) détection ampérométrique.

entraînait une erreur importante sur le dosage. Le retraitement journalier ou bijournalier des électrodes posant trop de problèmes pour des dosages s'effectuant en boîte à gants, cette méthode de détection a dû être abandonnée.

La méthode qui a été finalement retenue est l'ampérométrie à deux électrodes polarisées effectuée sur deux électrodes d'or amalgamé. La surface des électrodes est de 2,3 mm^2, la différence de potentiel appliquée entre les électrodes 20 mV. La figure 3-c représente un virage obtenu en ampérométrie. Le courant résiduel obtenu est de l'ordre de 0,2 μA. La détermination du point équivalent est faite graphiquement (*cf.* mode opératoire), ce qui entraîne une imprécision qui devient importante si on dose de petites quantités d'américium (prise d'essai < 1 μmole d'américium).

Malgré cet inconvénient, la méthode du "dead-stop end-point" a été retenue en raison de la bonne reproductibilité dans le temps de la réponse des électrodes et de sa facilité de mise en oeuvre.

Reproductibilité et justesse

Les résultats obtenus sont rassemblés dans le tableau 1. La reproductibilité des mesures est fonction de la prise d'essai. L'erreur relative moyenne sur le titre (σ) calculée au niveau de confiance de 95% est de $\pm 0{,}1\%$ pour des prises d'essai de 1,5 mg de néodyme et pour 700 μg d'américium et $\pm 0{,}15$ à 0,2% pour 350 μg (1,5 μmole) d'américium. Ces résultats sont à comparer à ceux obtenus par méthode indirecte (dosage volumétrique à l'EDTA avec détection spectrophotométrique du point équivalent) soit $\pm 0{,}5\%$ pour des prises d'essai de 5 mg d'américium par Yamamura[1] et $\pm 0{,}1\%$ au niveau de confiance de 68% pour des prises d'essai de 1 mg par Buijs et Bartscher.[4]

Tableau 1

Cation	Prise d'essai μg	Concentration moyenne trouvée, *mg/g*	Nombre de déterminations	Ecart type σ	Ecart moyen relatif %*
Nd	1500	9,159	12	0,015	$0{,}1_1$
Nd	450	1,512	11	0,003	$0{,}1_3$
^{241}Am	200 à 800	2,328	10	0,046	$0{,}1_0$
	700	2,329	9	0,0039	$0{,}1_3$
	300	2,327	9	0,0053	$0{,}1_7$
^{243}Am	350	2,323	8	0,0056	$0{,}2_5$
	80	2,338	4	0,0052	$0{,}3_5$

* Ecart moyen relatif % (σ mt) = $(\sigma\ t)/\sqrt{n} \times 100/\bar{x}$.

Les essais effectués sur de très faibles prises d'essai (80 μg) donnent une reproductibilité acceptable ($\sigma = \pm 0{,}35\%$) mais on constate l'apparition d'une dérive. Le résultat s'écarte de 0,7% par excès du résultat obtenu avec les prises d'essai plus importantes. Cette dérive due probablement au courant résiduel, ne peut être supprimée qu'en travaillant à concentration plus élevée en américium dans la cellule c'est à dire en utilisant une micro cellule.

Ne disposant pas d'américium étalon pour tester la justesse du dosage coulométrique, nous avons été amenés à effectuer des comparaisons avec d'autres méthodes de dosage.

Deux comparaisons ont été effectuées sur des solutions d'américium. La première portant sur une solution de ^{243}Am a consisté à comparer le dosage coulométrique à la mesure de l'activité alpha de la solution. On a obtenu les résultats suivants:

Dosage coulométrique: $2{,}208 \pm 0{,}004$ Mg/g en ^{243}Am.

Dosage par mesure activité alpha: $2{,}21 \pm 0{,}02$ Mg/g en ^{243}Am, (la période utilisée pour ^{243}Am est 7400 ans, l'incertitude sur la valeur de la période n'est pas prise en compte dans le calcul de l'incertitude sur le dosage par mesure de l'activité alpha).

Une autre comparaison a été effectuée avec la spectrométrie de masse à thermoionisation. Deux aliquotes, pesées avec précision, de solutions de ^{241}Am et ^{243}Am préalablement dosées par coulométrie, ont été mélangées et ce mélange a été analysé par spectrométrie de masse à thermoionisation afin de mesurer le rapport masse 241/masse 243. La valeur du rapport obtenu par spectrométrie de masse a été comparée à la valeur calculée à partir des titres coulométriques et des pesées. On a obtenu les valeurs suivantes:

241/243 valeur par coulométrie =
$$1{,}147 \pm 0{,}006$$
241/243 valeur par spectrométrie de masse =
$$1{,}146 \pm 0{,}005.$$

L'écart entre les deux valeurs (0,1%) indique une très bonne concordance entre les deux méthodes.

D'autres comparaisons effectuées sur des solutions de terres rares, avec des dosages gravimétriques, montrent que les résultats obtenus par coulométrie se trouvent toujours dans l'intervalle de confiance du résultat gravimétrique.

On notera également que l'activité alpha n'a pas d'influence sur la reproductibilité des mesures. En effet, les erreurs relatives sont comparables pour les dosages effectués sur des solutions de ^{241}Am et de ^{243}Am de concentrations voisines alors que les activités spécifiques de ces deux isotopes diffèrent d'un facteur de 17.

Eléments gênants

Les éléments gênants sont, soit des anions fortement complexants (citrate, fluorure...), soit des cations déplaçant le mercure de son complexe avec l'EDTA. Parmi ces derniers, il faut noter les terres rares; les métaux bivalents fortement complexés par l'EDTA ($\log K \geqslant 16$, Pb, Zn, Cd, Cu...), les métaux à la valence IV stable (Th, Zr, Pu...). Par contre, à pH 5, les alcalins, les alcalino-terreux, les platinoïdes, W, Ta, Mo,... ne gênent pas.

CONCLUSION

Malgré les limitations importantes apportées au champ d'application de la méthode par l'existence d'un grand nombre d'éléments gênants, le dosage coulométrique de l'américium garde tout son intérêt pour la préparation de solutions de référence et le dosage d'oxyde ou de métal pur. Ce dosage permet d'obtenir de bonnes précisions en utilisant peu de matière (σ mt $\pm$ 0,1% sur des prises d'essai de 700 μg; $\pm$0,2% sur des prises d'essai de 300 μg d'américium). Les résultats obtenus sont des résultats absolus ne nécessitant pas la préparation, la certification et la conservation de solution de référence, et par la même le dosage s'avère d'une grande rapidité de mise en oeuvre.

Le temps nécessaire à une détermination en boîte à gants avec ajout par pesée n'excède pas 1 h, ce qui permet d'effectuer 5 ou 6 déterminations dans une journée de travail.

La miniaturisation de la cellule de coulométrie et la préparation de micro électrodes permettant d'utiliser facilement la potentiométrie à courant imposé devraient permettre d'améliorer notablement les performances du dosage. Des essais en cours laissent espérer la possibilité de doser 100 μg d'américium avec une précision de $\pm$0,1 à $\pm$0,2%.

Remerciement—Les auteurs remercient Madame Poupard, Messieurs Cesario et Naudin pour les mesures par spectrométrie de masse ainsi que Messieurs Amoudry et Gendre pour les mesures d'activité alpha.

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Summary—A method is proposed for determination of americium by coulometry. It is based on displacement of mercury(II) from its EDTA complex by americium and its subsequent electroreduction. The equivalence point is found by the "dead-stop" method. The cell and apparatus described will give a precision of about 0.1% for 700 μg of americium and 0.2% for 300 μg (relative standard error of the mean, 95% confidence) under optimum conditions. The measurement is absolute and prior standardization is not required. The determination takes about an hour. The results are compared with those obtained by other methods and interferences have been studied.

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SPECTROPHOTOMETRIC DETERMINATION OF TETRAZENE IN PRIMERS AND PRIMER MIXES BY USE OF RESORCINOL

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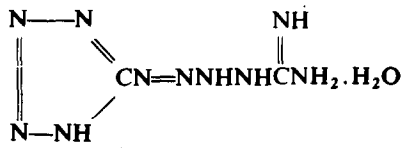
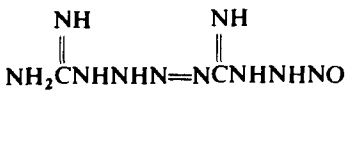
Summary—A spectrophotometric method is proposed for the determination of tetrazene (tetracene) in primers and primer mixes that involves treatment of the tetrazene with resorcinol solution and measurement of the intensity of the yellow colour of the diazo-dye produced. In the application of the method, lead styphnate and barium nitrate are first removed by extraction with ammonium acetate solution and then nitrocellulose and PETN are removed by extraction with acetone. The insoluble matter containing the tetrazene is boiled with resorcinol reagent, the solution filtered, and the absorbance measured at 400 nm. Conditions for optimum colour development are studied and the nature of the reaction is considered.

Tetrazene (tetracene), the explosive, is an important constituent of primers and priming compositions.

Tetrazene is now considered to be 1-tetrazene-2-carboximidamide,4-(1H-tetrazol-5-yl)-monohydrate (**I**).[1–3]* For about 45 years it had been considered to be 1-guanyl-4-nitrosoaminoguanylisotetrazene (**II**).[4–7]



I



II

Tetrazene in primers and primer mixes is usually determined (preferably in a 0.5-g sample) by dissolution of various ingredients in appropriate solvents, followed by collection on a crucible, weighing, treatment with boiling water to hydrolyse the tetrazene, filtration, reweighing, and taking the loss in weight to be tetrazene.[7] Another method consists of hydrolysing the tetrazene in dilute sulphuric acid and titrating with potassium bromate, with iodine in carbon tetrachloride as the indicator (the products of hydrolysis consume two equivalents of potassium bromate per mole).[8] Tetrazene in primers has also been determined polarographically, after dissolution in 0.01*M* hydrochloric acid and the addition of sodium tartrate[9] or after dissolution in 4*N* sulphuric acid and neutralization with tetramethylammonium hydroxide.[10] Qualitative identification of tetrazene in primers has been performed by infrared spectroscopy,[11,12] X-ray diffraction,[7,13,14] and microscopy.[5–7] A chemical qualitative test consists of dissolution of tetrazene in sodium hydroxide solution and addition of copper acetate to produce a blue precipitate.[5]

In the present work, a method was developed for the determination of tetrazene by boiling with resorcinol solution and measurement of the yellow colour produced.

EXPERIMENTAL

Reagents

All reagents used were of reagent grade.

Resorcinol solution (5%). Prepare fresh daily.

Ammonium acetate solution (20%), *water and acetone, saturated with tetrazene.* Add a few mg of tetrazene to 1 litre of the liquid to be saturated, shake, allow to stand overnight, and filter.

Tetrazene, military grade.[15] This is not commercially available, but readily synthesized in the laboratory.[1,3–6]

Determination of factor

Transfer the tetrazene (usually stored under water) to a 15-ml sintered-glass crucible, of fine porosity (porosity 4). Wash with water and then acetone. Dry by heating at 50° for 30 min. Weigh out duplicate portions (10–13 mg) into 150-ml beakers, using a balance that will give a precision of 0.1%. Add 60 ml of 5% resorcinol solution to each, cover with watch-glasses, heat to boiling, and boil moderately for 5 min. Run a reagent blank at the same time. Cool to room temperature and dilute to 1000 ml

* The IUPAC rules indicate that the name should be 4-carbamimidoyl-1-(1H-tetrazol-5-yl)tetrazene monohydrate.

in standard flasks. Measure the absorbance at 400 nm against the reagent blank and calculate the factor (average) as follows:

$$\text{Factor} = \frac{\text{mg of tetrazene}}{\text{absorbance}}$$

Procedure

Transfer 250 mg of the sample to a 15-ml sintered-glass crucible of fine porosity (porosity 4). Place the crucible in the adaptor of a suction flask, add 10 ml of 20% ammonium acetate solution saturated with tetrazene, and allow to stand for 10 min, stirring frequently with a rod. Turn on the suction, drain the crucible, and wash with portions of ammonium acetate solution until the washings are colourless (up to about 30 ml additional ammonium acetate solution will be required). Finally, wash with water saturated with tetrazene. Save the filtrate for the determination of lead and barium, if desired. Wash the crucible with acetone saturated with Tetrazene to remove nitrocellulose or pentaerythritol tetranitrate (PETN) and determine these substances if desired. Place the crucible on its side in a 150-ml beaker and add 60 ml of 5% resorcinol solution. Cover with a watch-glass, heat to boiling, and boil moderately for 5 min while stirring frequently with a rod and rotating the crucible. Rinse the crucible with water, filter the solution through the same crucible, and wash with water. Dilute the filtrate to 1000 ml in a standard flask and measure the absorbance at 400 nm against the reagent blank. Calculate the per cent tetrazene as follows:

$$\%\ \text{Tetrazene} = \frac{\text{absorbance} \times \text{factor} \times 100}{\text{mg of sample}}$$

Note. For smaller size samples (25–125 mg) proceed as above but dilute in a smaller standard flask (100–500 ml) so that the tetrazene content will be about 0.010–0.013 mg/ml. Calculate the per cent tetrazene as follows:

$$\%\ \text{Tetrazene} = \frac{\text{absorbance} \times \text{factor} \times \text{ml of diluted solution}}{\text{mg of sample} \times 10}$$

DISCUSSION AND RESULTS

Study of factors affecting the colour

The effect of different amounts of 5% resorcinol solution (10.0 mg of tetrazene, 3 min boiling time, dilution to 1000 ml) is shown in Table 1. The colour develops fully with 10 ml of 5% resorcinol solution and does not change significantly with greater amounts. The use of 60 ml of resorcinol solution is recommended, since this is nearly enough to cover the sintered-glass crucible placed on its side in a 150-ml beaker.

The effect of boiling time is shown in Table 2. The colour develops fully after boiling for about 2 min and decreases slightly on boiling for 30 min. A 5-min boiling period is recommended.

Table 1. Effect of amount of 5% resorcinol solution (10.0 mg of tetrazene, 3 min boiling, dilution to 1000 ml)

Resorcinol solution, *ml*	Absorbance
2	0.33
5	0.40
10	0.42
25	0.41
50	0.42
100	0.43

Table 2. Effect of boiling time (10.0 mg of tetrazene, 60 ml of 5% resorcinol solution, dilution to 1000 ml)

Boiling time, *min*	Absorbance
Incipient boiling	0.36
2	0.43
5	0.42
15	0.42
30	0.41

The absorption spectrum in the visible region shows just one peak with maximum absorbance around 400 nm. It is recommended that the absorbance be measured at this wavelength. The proposed method is not useful in the ultraviolet because resorcinol absorbs strongly in that region. The colour is stable for several hours.

A calibration curve, prepared by weighing out portions of tetrazene (5–15 mg) and proceeding as in the method, was found to be a straight line. However, weighing small amounts of tetrazene is tedious, so the use of a factor, rather than a calibration curve, is recommended. The colour is not affected by excess of resorcinol, so the final volume chosen does not alter the absorbance for a given concentration of tetrazene.

Interferences

In considering the question of interferences, it was borne in mind that the proposed method was

Table 3. Reaction of resorcinol solution with constituents of explosives

Constituent	Reaction
Lead styphnate	Partially soluble, yellow solution
Barium nitrate	Soluble, colourless solution
PETN	Insoluble, colourless solution
Nitrocellulose	Insoluble, colourless solution
Antimony trisulphide	Insoluble, colourless solution
Aluminium	Slightly soluble, colourless solution
Calcium silicide	Insoluble, colourless solution
TNT	Partially soluble, slight pink colour
RDX	Insoluble, colourless solution
Tetryl	Partially soluble, slight yellow colour
Lead thiocyanate	Soluble, slight yellow colour
Lead azide	Insoluble, colourless solution
Sodium azide	Soluble, colourless solution
Lead dioxide	Partially soluble, yellow solution
Potassium chlorate	Soluble, colourless solution
2,4-Dinitrotoluene	Partially soluble, slight green colour
Diphenylamine	Insoluble, colourless solution
2-Nitrodiphenylamine	Partially soluble, yellow colour
Ethyl centralite	Partially soluble, yellow colour
Nitroguanidine	Partially soluble, colourless solution
Gum arabic	Soluble, colourless solution
Butyl phthalate	Insoluble, colourless solution

designed for small arms lead styphnate primers. This type of primer ordinarily contains lead styphnate (about 35–40%), barium nitrate (about 35–45%), varying smaller percentages of other ingredients (such as antimony trisulphide, nitrocellulose, PETN, powdered aluminium, and calcium silicide), and 2–5% tetrazene.

A study was made of the effect of boiling the resorcinol solution with different ingredients of explosives. The results (Table 3) shows that the colour reaction with resorcinol is selective for tetrazene, but there are interferences from insoluble matter, colour from the explosive ingredients, and colour due to oxidation of the resorcinol (by lead dioxide).

The interference of lead styphnate was eliminated by extraction with ammonium acetate solution (this also removes barium nitrate). Even though nitrocellulose and PETN do not interfere, it was decided to extract these compounds with acetone so that they could be determined [tetryl, TNT, and cyclotrimethylenetrinitramine (RDX) would also be extracted]. The interference from the insoluble antimony trisulphide, aluminium powder and calcium silicide was eliminated by filtration.

Tetrazene is considered to be completely insoluble in water, ammonium acetate solution, and common organic solvents.[5–7] However, in order to avoid any possibility of error, it is recommended that the water, ammonium acetate solution and acetone used be saturated with tetrazene.

Attempts were made to eliminate the interference of lead dioxide (which is found in some primers) by treatment with 20% ammonium acetate solution containing a little hydrogen peroxide. It was found that lead dioxide (together with lead styphnate and barium nitrate) dissolved in this solvent but some tetrazene also dissolved, so the results were low. It might be possible to establish a correction factor, but this was not investigated.

The possible application of the method to the determination of tetrazene in lead styphnate–lead azide primers was not investigated. Lead azide does not give a colour with resorcinol solution (Table 3) and also is readily soluble in ammonium acetate solution,[7] so presumably it would not interfere.

In primer analysis, it is customary to determine several ingredients consecutively, on one or two samples, since the amount of sample available is frequently small.[7,9] The proposed method for tetrazene fits into such a scheme, since the different ingredients (after treatment with the different solvents) can be determined by the usual classical, spectrophotometric and atomic-absorption methods, or calculated by difference.

Chemistry of the reaction

Tetrazene is made by the diazotization of aminoguanidine with sodium nitrite (in a nearly neutral medium).[1,3–6] It might be expected, therefore, that tetrazene, like other diazo-compounds, would couple with certain aromatic compounds to produce dyes. Mention has been made of dyes produced by reaction of tetrazene with α-naphthol, β-naphthol and aromatic amines.[16–18] In the usual preparation of these dyes, an aqueous suspension of the tetrazene is treated with a solution of the aromatic compound, the mixture is heated at 80° for 25 min, and the dye is precipitated by adding hydrochloric acid.[16]

The exact nature of the reaction involved in the formation of the dye from resorcinol is uncertain. However, judging by the work of past investigators on naphthols and amines,[17,18] the reaction probably which immediately reacts with the resorcinol to produce the dye (possibly 1,2,3,4-tetrazole-5-azo-4-resorcinol). It has been stated[17,18] that in the absence of a coupling agent the diazotetrazole loses two atoms of nitrogen to form hydroxytetrazole, a compound that does not react to produce a dye. This explains our observation that the intensity of the colour was lower if the tetrazene were hydrolysed by boiling with water before the resorcinol was added. The longer the boiling time before the addition of the resorcinol, the greater was the decrease in the intensity of the colour.

Resorcinol was chosen as the coupling reagent (in preference to other phenolic compounds and amines) because it gave a low blank.

Results for primer mixes and primers

The results obtained for tetrazene in several syn-

Table 4. Results for tetrazene in synthetic primer mixes (1000 ml dilution)

Present, *mg*		Tetrazene found, *mg*
6.2	Tetrazene + 100 Pb styphnate + 100 $Ba(NO_3)_2$ + 20 Sb_2S_3	6.4
9.6	Tetrazene + 100 Pb styphnate + 100 $Ba(NO_3)_2$ + 20 Sb_2S_3	9.8
12.7	Tetrazene + 90 Pb styphnate + 90 $Ba(NO_3)_2$ + 20 Sb_2S_3 + 20 nitrocellulose	12.9
10.5	Tetrazene + 90 Pb styphnate + 90 $Ba(NO_3)_2$ + 20 Sb_2S_3 + 20 $CaSi_2$	10.2
12.0	Tetrazene + 90 Pb styphnate + 90 $Ba(NO_3)_2$ + 20 Sb_2S_3 + 20 PETN + 20 Al powder	12.1
6.8	Tetrazene + 90 Pb styphnate + 90 $Ba(NO_3)_2$ + 20 Sb_2S_3 + 20 PETN + 20 Al powder	7.1

thetic primer mixes are shown in Table 4. The recoveries were good. The results obtained on an actual primer (containing lead styphnate, barium nitrate, antimony trisulphide, aluminium powder, PETN, and nominally 3% tetrazene) were 3.05 and 3.14%. There was insufficient sample to analyse the primer for tetrazene by an alternative method.

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OXIDATION OF SULPHIDE MINERALS—VI*

FERROUS AND FERRIC IRON IN THE WATER-SOLUBLE OXIDATION PRODUCTS OF IRON SULPHIDE MINERALS

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Summary—A pseudo-kinetic method has been developed for determining the ferrous and ferric iron in the water-soluble oxidation products of pyrrhotite, pyrite and chalcopyrite, and ores and concentrates containing them. Two determinations are required for each material. In one, the total iron is determined with 1,10-phenanthroline after reduction to Fe(II). In the other, the reduction of Fe(III) is retarded by complexation with fluoride. The difference in the amount of ferrous phenanthranoline complex produced in these two determinations is a function of the original Fe(III) concentration and of time.

As part of a general study of the long-term stability of sulphide-bearing ores and concentrates of the Canadian Certified Reference Materials Project, the air-oxidation of the more common sulphide minerals was investigated. Analytical methods were developed to determine the total metal[1–3] and the sulphur-bearing constituents[4] in the oxidation products of sulphide minerals. The application of these methods has allowed the definition of the oxidation products of pyrite, chalcopyrite and pyrrhotite[5] and of galena, sphalerite and chalcocite.[6]

Although the total metal in the oxidation products of a sulphide mineral is an excellent indication of the extent of oxidation, it gives little information concerning the distribution of the metal among the various possible products. For example, for a mineral such as pyrrhotite which can oxidize to goethite, $Fe_2O_3 \cdot H_2O$, and to $FeS_2O_3 + Fe_2(SO_4)_3 \cdot xH_2O$, a total metal value does not indicate whether the products are separate entities, combined in a basic sulphate or combined in an even more complex fashion. Indeed, some samples of oxidized pyrrhotite exhibit a blue colour resembling that of certain materials, *e.g.*, tourmaline, and partially oxidized vivianite, in which Fe(II) → Fe(III) charge transfer is thought to occur.[7] It is evident that our understanding of oxidation would be improved by knowledge of the nature as well as the chemical composition of the oxidation products of a sulphide mineral.

This communication reports an initial attempt to obtain information on the nature of the oxidation products of the iron sulphide minerals, by use of chemical phase analysis.[8] A method is described for the determination of Fe(II) and Fe(III) in the water-soluble oxidation products of pyrite, chalcopyrite and pyrrhotite. The determination of the total iron, *i.e.*, Fe(II) + Fe(III), is straightforward. The Fe(II) and Fe(III) components must, however, be determined by a pseudo-kinetic procedure because of the strongly reducing properties of the unoxidized sulphide mineral substrate.

EXPERIMENTAL

Reagents

1,10-Phenanthroline (phen) solution, 1.5% in ethanol, (100 ml ethanol.)

Hydroxylamine hydrochloride solution 10%.

Buffer pH 2.8, Dissolve 94.5 g of monochloroacetic acid and 20.0 g of sodium hydroxide in water and dilute to 1 litre.

Ammonium fluoride solution, 7.5%.

Mineralogical materials

Pyrrhotite (Falconbridge, Ontario, Canada, 59.94% Fe).
Pyrite (Rico, Colorado, U.S.A., 46.18% Fe).
Chalcopyrite (Ajo, Arizona, U.S.A., 30.01% Fe).

All mineral samples had a grain size between 325 and 200 mesh (Tyler) and were treated with 10*M* phosphoric acid[1] and ammonium sulphide solution[5] to remove oxidation products formed during their preparation from coarse lumps. Portions of these samples were oxidized for various periods of time at various temperatures and relative humidities.

Procedure

Pipette into each of two 100-ml flasks, 36 ml of water, 5 ml of pH-2.8 buffer, 1 ml of hydroxylamine hydrochloride solution and 4 ml of phen solution. Add an additional 4 ml of water to one flask and 4 ml of ammonium fluoride solution to the other. Using a small funnel, transfer to each flask 50–1000 mg of mineral, expected to contain not more than about 400 μg of water-soluble iron†. Using a mechanical shaker, agitate the stoppered flasks for 15 min at room temperature. Centrifuge a small portion from each flask, decant the clear red solution into a dry 1-cm cuvette and measure the absorbance at 510 nm against a water blank. Return the contents of the cuvette and any solution remaining in the centrifuge tube to the 100-ml flask. Repeat

† The amounts of sample added to the flasks should be as similar as possible, with minimum elapse of time between additions.

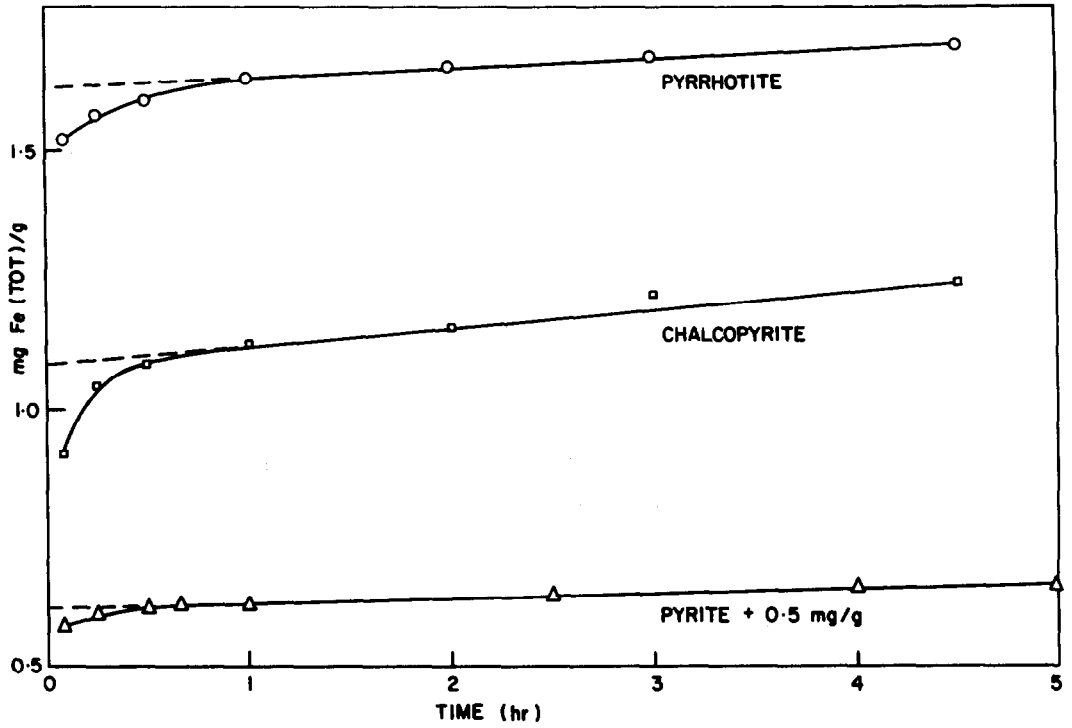

Fig. 1. Iron in the water-soluble oxidation products of pyrrhotite, chalcopyrite and pyrite, as a function of time.

this procedure to give total agitation times of 30, 60, 90 and 120 min.

The iron content of the solution is determined from the calibration curve.

Calibration curve

A calibration curve is constructed with a ferrous ammonium sulphate solution containing about 100 mg of iron per litre. Aliquots of this stock solution are transferred to 50-ml flasks containing 5 ml of pH-2.8 buffer, 1 ml of hydroxylamine hydrochloride solution and 4 ml of phen solution. The contents are diluted to the mark and the absorbance is read at 510 nm.

RESULTS AND DISCUSSION

Iron must be in solution to form the phen complex. Therefore, only those iron-bearing species that are soluble in water or in pH-2.8 chloroacetic acid buffer, *e.g.*, FeS_2O_3, $FeSO_4$, $Fe_2(SO_4)_3$, *etc.*, will be determined by the proposed method. As expected, tests with Fe_2O_3 and Fe_3O_4 (reagent grade) showed no solubility in water or acetic acid buffer for contact times up to 4.5 hr, which is longer than required for the proposed method. In view of the observation that the chloroacetic acid buffer does not leach iron oxides, it can be concluded that any iron that is leached by the buffer is essentially the same as that leached by water alone, *i.e.*, the proposed method determines the ferrous and ferric iron in the water-soluble oxidation products.

Addition of hydroxylamine hydrochloride

In the absence of a reducing agent such as hydroxylamine, any Fe(III) in the water-soluble oxidation products is rapidly reduced to Fe(II) by the sulphide mineral itself. This reduction, of course, releases additional iron into solution so that the total iron values obtained are high. Results obtained so far indicate that one mole of Fe(III) releases an additional 0.25 mole of iron from pyrrhotite but only 0.13 mole from pyrite or chalcopyrite. This difference is, of course, a result of the different Fe:S ratios in these minerals. Because this problem of high total iron values is easily overcome by the addition of a reducing agent such as hydroxylamine, further investigation was not undertaken.

Effect of leaching time

Figure 1 shows the effect of agitation or leaching time, t, on the total iron values obtained for samples of pyrrhotite, pyrite and chalcopyrite. The rate of increase of colour formation is obviously essentially linear after approximately 1 hr.

The slope of the linear portion of the curves suggests that there is slight further attack on the non-water-soluble oxidation products or perhaps on the unoxidized mineral itself. It seems reasonable, in analogy with copper in the chalcopyrite system,[3] that extrapolation of the linear portion to $t = 0$ be used to obtain the total iron value for the water-soluble oxidation products.

Complexation of ferric iron

The determination of the Fe(III) in the water-soluble oxidation products requires that this species be protected from reduction to Fe(II) by the minerals

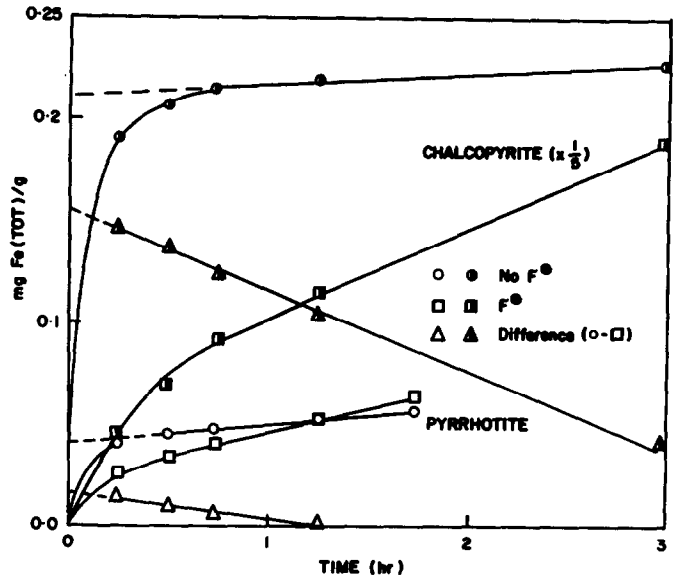

Fig. 2. Iron in the water-soluble oxidation products of pyrrhotite and chalcopyrite, as a function of time, when determined in presence and absence of fluoride.

or by the added hydroxylamine. Complete prevention of such reduction is, however, not possible. Of several complexing reagents tested for stabilizing Fe(III), fluoride was the most satisfactory. The fluoride complexes of Fe(III) are reduced to Fe(II) at a sufficiently slow rate and in addition do not absorb at 510 nm. These two facts provide the basis for kinetic differentiation of iron(III) from iron(II).

Determination of ferrous and ferric iron

Figure 2 shows a plot of typical results obtained by the proposed method for a sample of unoxidized pyrrhotite and a sample of chalcopyrite oxidized at 50° and 75% relative humidity (RH) for 5 weeks. The effect of the fluoride complexation of Fe(III) on the total iron values is obvious. The difference between the total iron values determined with and without fluoride present (ΔFe) has been found to be a linear function of reaction time for all the samples of chalcopyrite and pyrite but only about half of the samples of pyrrhotite so far analysed. The plot of this difference *vs.* time is, in fact, a plot of the change in the Fe(III) concentration with time. Theoretically, therefore, extrapolation to $t = 0$ should give the true value of Fe(III) in the water-soluble oxidation products.

The total iron is given by extrapolation (to $t = 0$) of the essentially linear portion of the plot of total iron (determined in absence of fluoride) *vs.* t. The Fe(II) is then given by subtracting the iron(III) value from the total iron.

To determine whether the procedure yields the correct values when the relationship between ΔFe and t is linear, samples of clean pyrrhotite, chalcopyrite and pyrite were spiked with known amounts of Fe(II) and Fe(III). The results given in Table 1 clearly show that the method is capable of determining Fe(II) and Fe(III) in the water-soluble oxidation products of the iron sulphide minerals.

Leaching action of fluoride solution

Fluoride solution, because of its ability to complex Fe(III), is a potential solvent for Fe(III) compounds

Table 1. Determination of known quantities of Fe(II) and Fe(III)

Fe added, *mg*		Fe found, *mg*			
Fe(II)	Fe(III)	Fe(II) total	Fe(II) net	Fe(III) total	Fe(III) net
Pyrrhotite					
0.0	0.0	0.03	0.0	0.03	0.0
0.12	0.18	0.14	0.11	0.22	0.19
0.0	0.31	0.03	0.0	0.33	0.30
Chalcopyrite					
0.0	0.0	0.01	0.0	0.01	0.0
0.12	0.18	0.14	0.13	0.21	0.20
0.0	0.31	0.02	0.01	0.33	0.32
Pyrite					
0.0	0.0	0.003	0.0	0.003	0.0
0.12	0.18	0.11	0.11	0.19	0.19
0.0	0.31	0.00	0.00	0.30	0.30

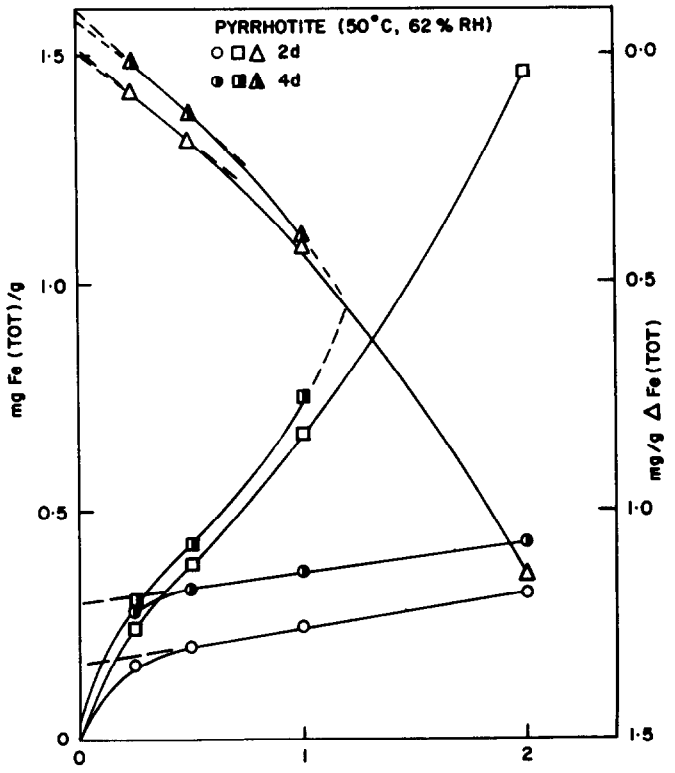

Fig. 3. Iron in the water-soluble oxidation products of pyrrhotite, as a function of time, when determined in the absence and presence of F^-. (N.B. The △ and ▲ points are referred to the right-hand scale.)

that are not soluble in water. Indeed, determinations on some samples of oxidized pyrrhotite gave a larger value for total iron when fluoride was present than when it was absent, indicating that the fluoride promoted dissolution of water-insoluble oxidation products. Figure 3 illustrates the results obtained for pyrrhotite oxidized at 50° and 62% RH for 2 and 4 days. The non-linear relationship between ΔFe and t is evident and the extrapolation of these plots to $t = 0$ is somewhat more difficult (note that the scale on the right-hand side of the figure refers to ΔFe, and is inverted relative to the scale on the left-hand side). A non-linear regression fit to the data would yield the best results but the assumption that the relation is linear for the lowest values of t would cause only a small and acceptable error when deviation from linearity is not too great, as is observed in Fig. 3.

To determine whether non-linear plots of ΔFe *vs.* t are capable of yielding correct values of total Fe, Fe(III) and Fe(II), samples of pyrrhotite oxidized at 50° and 62% RH for 1, 4 and 7 days were spiked with known amounts of Fe(II) and Fe(III). The results are shown in Table 2 and again illustrate that the proposed method is capable of determining the Fe(III) and Fe(II) content of the water-soluble oxidation products of the iron sulphide minerals.

Table 2. Determination of known quantities of Fe(II) and Fe(III) added to pyrrhotite oxidized at 50°C and 62% RH

Oxidized for	Fe added, *mg*		Fe found, *mg*			
	Fe(II)	Fe(III)	Fe(II) total	Fe(II) net	Fe(III) total	Fe(III) net
1 day						
	0.0	0.0	0.01	0.0	0.0	0.0
	0.12	0.18	0.13	0.12	0.19	0.19
	0.0	0.31	0.01	0.0	0.32	0.32
4 days						
	0.0	0.0	0.05	0.0	0.03	0.0
	0.12	0.18	0.18	0.13	0.20	0.17
	0.0	0.31	0.05	0.0	0.35	0.32
7 days						
	0.0	0.0	0.07	0.0	0.05	0.0
	0.12	0.18	0.19	0.12	0.24	0.19
	0.0	0.31	0.07	0.0	0.36	0.31

Table 3. Fe(II) and Fe(III) in water-soluble oxidation products of chalcopyrite oxidized at 50°C and 75% RH for 5 weeks

Sample, *g*	Fe(II), *mg/g*	Fe(III), *mg/g*
0.3013	0.28	0.78
0.3032	0.28	0.73
0.3007	0.26	0.78
0.1507	0.29	0.76
0.0550	0.26	0.75
	$s = 0.03$	$s = 0.04$

Reproducibility

This was tested with the sample of chalcopyrite oxidized at 50° and 75% RH for 5 weeks. The results of quintuplicate determination of Fe(II) and Fe(III) in the water-soluble oxidation products of this sample are summarized in Table 3. The observed precision is well within that expected in chemical phase analysis.[8] Moreover, some variability is to be expected in the subsampling of the oxidized chalcopyrite sample.

Applicability of method

The method overcomes the problem of reduction of Fe(III) by the mineral itself. It can therefore probably be applied to concentrates and ores containing pyrrhotite, pyrite and chalcopyrite as well as other iron minerals, *e.g.*, arsenopyrite, FeAsS, bornite, Cu_5FeS, *etc.* Application of this method to oxidized coals[9] and soils[10] containing pyrite also seems possible. Moreover, because Fe(III) is easily reduced by any sulphide mineral present, the proposed method can be used for the analysis of the water-soluble iron phases from oxidized minerals such as sphalerite which are, in general, iron-bearing.

The floatability of a sulphide-bearing ore can vary with the extent of oxidation. Water-soluble oxidation products probably pass into solution rapidly and should not affect the floatability. Therefore, any observed difference in the flotation behaviour between samples of the same ore is probably due to different concentrations of the water-insoluble oxidation products. For ores containing the iron sulphide minerals, the difference between the total iron in the oxidation products[1] and that in the water-soluble oxidation products should be a good indicator of a difference in the extent of oxidation of samples of that ore.

A knowledge of the Fe(II) and Fe(III) content of the water-soluble oxidation products of iron sulphide minerals can provide some information on the nature

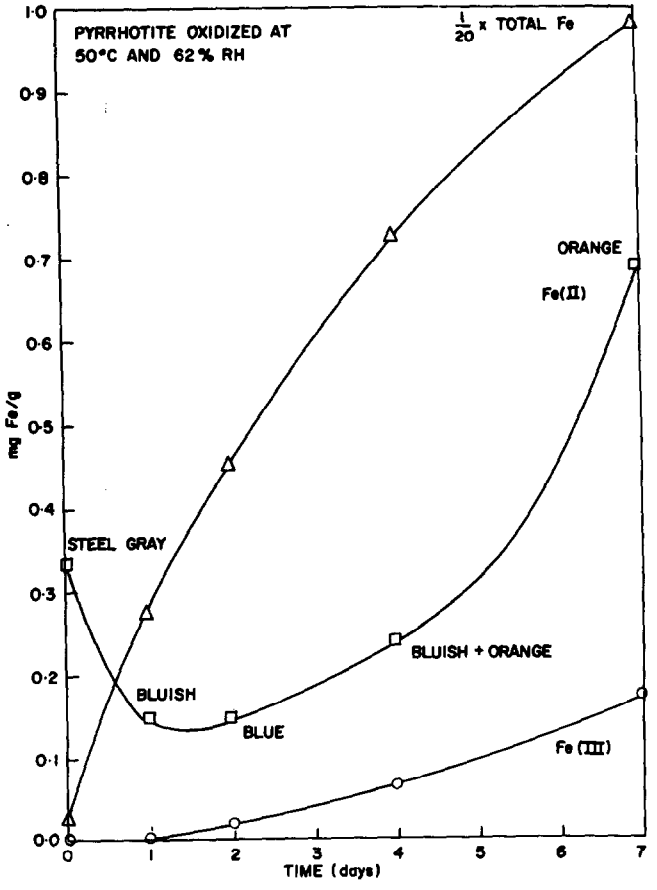

Fig. 4. Total iron in all oxidation products and Fe(II) and Fe(III) in the water-soluble oxidation products of samples of pyrrhotite, as a function of time of oxidation at 50°C and 62% RH.

of those products. Figure 4 shows a plot of the Fe(II) and Fe(III) values in the water-soluble oxidation products, and the total iron in the oxidation products,[1] for samples of pyrrhotite that had been oxidized at 50° and 62% RH for up to 7 days. Each sample was kept at controlled temperature and humidity at all times, except when subsamples were being removed.

Figure 4 also gives the colour of the test samples. The change in colour of the pyrrhotite specimen is indicative of the changing composition of the surface layer or, possibly, of all of the oxidation products. Goethite, $Fe_2O_3 \cdot H_2O$, and $Fe_2(SO_4)_3 \cdot xH_2O$ are orange or beige and are the oxidation products of pyrrhotite oxidized for 7 days.[5] Goethite is expected to be predominant at 50° and 62% RH.[5] The spectrum of the blue subsample oxidized for 2 days (not shown) suggests a mixed oxidation state iron complex in an oxygen matrix, with Fe(II) → Fe(III) charge-transfer bands giving rise to the blue colour.[7]

For pyrrhotite, the Fe(II)-containing oxidation products, thought to be mainly FeS_2O_3, remain essentially the same as the extent of oxidation increases.[5] It is evident, therefore, that any binding of Fe(II) as a less soluble product of more complex nature, such as by formation of a blue mixed oxidation state iron compound should result in a decrease in amount of water-soluble Fe(II)-containing oxidation products. Figure 4 clearly illustrates that the variation in the Fe(II) content of the water-soluble oxidation products follows in the expected fashion the formation and subsequent transformation of the mixed oxidation state iron compound. In contrast, the total iron content of all oxidation products shows an increase with the extent of oxidation, but this increase provides no information concerning the nature of the oxidation products. A more detailed interpretation of the variation of the Fe(II) and Fe(III) content of the water-soluble oxidation products with the extent of oxidation is beyond the scope of this communication.

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SPARK-SOURCE MASS-SPECTROMETRIC SENSITIVITY FACTORS FOR ELEMENTS IN A GRAPHITE MATRIX

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Summary—Relative sensitivity factors for determination of 41 elements by spark-source mass-spectrometry have been measured. The samples were pressed into graphite electrodes and ionized with a radiofrequency spark. The mass spectra were recorded on a photoplate and the resulting data processed by a computer. Indium was used as standard and the relative sensitivity factors for both singly- and doubly-charged ions were determined with reference to the singly-charged indium ion, with an overall error of 30%. The mean analysis precision was 16%.

Owing to the very high ionization energy used in the spark plasma, spark-source mass-spectrometry (SSMS) is a multielement analysis technique with comparable sensitivity for all elements from light to heavy. It can be used over a large concentration range so it is a very useful technique for semiquantitative survey analyses of widely different materials (without correction factors). The usefulness of SSMS can be improved by introducing so-called elemental relative sensitivity factors.

The ion-beam reaching the mass analyser after extraction from the ion-source is not representative of the electrode composition because of selective evaporation and ionization, and non-uniform extraction. In instruments without z-focusing the transmission through the analyser is different for every mass. Differences in detector response also play a major role.[1] The difference between the measured and true concentration of an element (x) may be compensated for by the use of a sensitivity factor which is defined relative to an internal standard element (y) as:

$$R(x/y) = (C_x/C_y)_{meas}/(C_x/C_y)_{true} \quad (1)$$

The relative sensitivity factor of the internal standard element itself is unity, so equation (1) reduces to:

$$R(x/y) = \frac{C_{x\,meas}}{C_{x\,true}}. \quad (2)$$

The sensitivity factors are experimentally determined with standard reference materials.

Sensitivity factors will be affected by the method of calculation, depending on which corrections are included, by the instrument settings and by the detector system used (photographic or electric). Literature data on relative sensitivity factors are difficult to compare because of incomplete descriptions of the experimental conditions.[2] The question of whether relative sensitivity factors depend on the matrix has been discussed recently.[3,4,5]

In this paper relative sensitivity factors are reported for photographic detection of 41 elements in a graphite matrix.

EXPERIMENTAL

Apparatus

The mass spectrometer used was a radiofrequency spark-source double-focusing instrument with Mattauch-Herzog geometry (JMS-01 BM-2, JEOL, Tokyo). It has a spherical electric field for focusing the ion-beam in the z-direction. Ilford Q-2 38 cm × 5 cm ion-sensitive plates were used as detectors. The transmittance of the exposed plates was measured with a single-beam microdensitometer (JEOL JMD-2C) controlled by a JEOL-JEC-6 minicomputer. Photoplate measurement data were punched on paper tape and processed off-line by a 64-K computer (PDP 11/45). The automated evaluation of photographically recorded mass spectra is fully described elsewhere.[6] Recently the microdensitometer and the larger computer were linked by magnetic tape, instead of the minicomputer and paper tape, thus reducing the processing time from about 160 to 90 min for one photoplate with 15 exposures.[7]

Sample preparation

Since only an extremely small part of the electrode material reaches the detector in SSMS analysis, the homogeneity requirements for the sample are very stringent. The most widely used method for preparing graphite electrodes is the freeze-drying of a suspension of graphite powder in the standard metal solution and subsequent pressing to form the electrodes.[8,9,10] In this work standard metal solutions (Johnson–Matthey suprapure metal oxides dissolved in Merck suprapure acids or bases and demineralized doubly distilled water) were mixed with ultrapure graphite (Johnson–Matthey), with acetone as wetting agent, in a film evaporator (Büchi Rotavapor M-HB 140). The 25-ml flask, positioned at a 45° angle, rotates around its axis and the suspension is dried under vacuum at a temperature of about 45°. The dried graphite is then shaken for 5 min in a Wig-L-Bug shaker and pressed into electrodes (12 mm long, 2 mm diameter) under a pressure of 10 ton/cm^2.

Mass spectrometric procedure

Indium was chosen as the internal standard because its concentration in common environmental samples is very

Table 1. Instrumental settings for SSMS-analysis of graphite electrodes

Spark: radiofrequency	1 MHz
spark voltage	40 kV
pulse length	20 μsec
repetition frequency	1 kHz
Width of the slits: main slit	10–20 μm
α-slit	0.6 mm
β-slit	0.8 mm
Analysis: accelerating voltage	28 kV
electrostatic sector voltage	2.9 kV
magnetic field	14000 gauss
Vacuum: source	$< 1 \times 10^{-7}$ mmHg
analyser	$< 1 \times 10^{-8}$ mmHg
Plate development: temperature	18°
developing time	2.5 min
fixation time	5 min

Table 2. Relative sensitivity factors in a graphite matrix for singly-charged ions with reference to indium

Element	Measured relative sensitivity factor This work	Hamilton and Minski[9]	Konishi[12]	Conzemius and Svec[13]
Sc	0.24 ± 0.18 (3)*			
V	0.41 ± 0.17 (10)	0.62	0.40	
Mn	0.58 ± 0.13 (10)	0.67	0.58	
Fe	0.59 ± 0.16 (6)	1.0	0.48	
Co	0.52 ± 0.09 (14)	0.57	0.47	
Ni	0.59 ± 0.11 (8)		0.29	
Cu	0.58 ± 0.11 (12)		0.36	
Zn	0.61 ± 0.07 (7)	0.52	0.44	
As	0.36 ± 0.08 (13)		0.42	
Se	0.34 ± 0.08 (9)	0.39	0.27	
Rb	2.14 ± 0.65 (4)	3.4	1.4	
Sr	0.48 ± 0.05 (5)	1.0	0.60	
Y	0.21 ± 0.02 (4)			0.21
Zr	0.17 ± 0.02 (7)	0.14	0.20	
Mo	0.22 ± 0.07 (6)	0.27	0.29	
Pd	0.62 ± 0.32 (6)			
Ag	1.07 ± 0.25 (17)	0.46	0.48	
Cd	0.26 ± 0.05 (6)	0.21	0.29	
In	1	1	1	
Sb	0.30 ± 0.03 (6)		0.31	
Te	0.25 ± 0.05 (5)	0.27	0.26	
Ba	0.34 ± 0.14 (7)	0.38	0.56	
La	0.19 ± 0.07 (7)			0.19
Hf	0.19 ± 0.15 (2)	0.19		
W	0.15 ± 0.04 (7)	0.14	0.16	
Re	0.24 ± 0.06 (11)			
Au	0.32 ± 0.15 (6)			
Hg	0.09 ± 0.08 (3)		0.11	
Pb	0.21 ± 0.03 (14)	0.24	0.45	
Bi	0.18 ± 0.02 (8)	0.20	0.34	
Nd	0.15 ± 0.02 (5)			0.24
Sm	0.43 ± 0.12 (2)			0.34
Eu	0.28 ± 0.08 (6)			0.42
Gd	0.32 ± 0.11 (6)			0.22
Tb	0.19 ± 0.04 (10)			0.20
Dy	0.17 ± 0.03 (6)			0.22
Ho	0.21 ± 0.05 (5)			0.24
Er	0.22 ± 0.07 (5)			0.24
Yb	0.19 ± 0.21 (2)			0.43
Lu	0.18 ± 0.02 (5)			0.17
U	0.11 ± 0.02 (19)	0.19	0.19	

* Figures in brackets refer to the number of measurements.

low, so systematic errors are at a minimum. It has only two stable isotopes (^{115}In, 95.72% and ^{113}In, 4.28%) and singly- and multiply-charged ions cause very few spectral interferences. Its low boiling point (2000°) and low first ionization energy (5.77 eV) make indium a sensitive element for SSMS analysis.

The cylindrical electrodes were positioned top-to-top,[11] with one electrode fixed and the other vibrating, to maintain a mean gap of about 300 μm. The instrumental parameters are listed in Table 1. A series of 15 graded exposures was made on each plate, ranging from 0.1 to 150 nC. All samples were presparked for at least 5 min.

Fifteen different standard samples were prepared, containing altogether 42 different elements in concentrations between 10 and 40 ppM. The data presented were extracted from 20 photoplates, giving 870 measured values for concentrations of singly-charged ions (matrix ions excluded) or 319 mean element concentration values. In addition 190 mean concentrations were measured by means of doubly-charged ions.

RESULTS AND DISCUSSION

For analytical purposes it is necessary to have a factor which relates the measured to the true elemental concentration. A physical or chemical interpretation of this factor is not necessarily required. In the computer evaluation of the mass spectra in this work, no correction was made for differences in plate sensitivity with differences in ion mass, energy or structure. The elemental relative sensitivity factors listed below consequently contain contributions from all fundamental sensitivity-determining phenomena.

Relative sensitivity factors for singly charged ions

Column 2 in Table 2 lists the mean sensitivity factors vs. the indium standard for 40 elements. These factors were obtained by calculating elemental concentrations from the photoplates, assuming equal sensitivity for each atom in the mass spectrometer and comparing this value with the true concentration in the sample. The confidence limit of the mean (also given in column 2) is a measure of the accuracy of the determination of the sensitivity factor and is defined by:

$$A = t\sqrt{\frac{\sum_i (R_i - \bar{R})^2}{n(n-1)}} \qquad (3)$$

where R_i and $\bar{R}$ are the individually measured and mean sensitivity factors respectively, n the number of measurements for the element and t the Student-t factor for two-tailed 90% confidence.

Our experimental data are compared with literature data from Hamilton and Minski,[3] Konishi[12] and Conzemius and Svec[13] in columns 3, 4 and 5 of Table 2. The precision of the measurement is defined by the coefficient of variation:

$$S\% = \frac{100}{\bar{R}} \cdot \sqrt{\frac{\sum_i (R_i - \bar{R})^2}{n-1}}$$

The mean precision for all the data is 27%. The measurements were carried out over a period of 19 months. The mean precision over a shorter series is better, 16%, probably because of more constant instrumental settings.

Hamilton and Minski[9] and Conzemius and Svec[13] used an AEI-MS7 and Konishi[12] a CEC 21-110B mass spectrometer, both without z-focusing and with short photoplates (25 cm). In their spectrum calculation, line-width correction was performed by using the line-width at half maximum intensity instead of integration. The calculation algorithm of Konishi[12] also included a correction factor for the mass-dependence of the emulsion sensitivity ($m^{-0.4}$). In order to make comparison with the other data possible, these sensitivity factors have been recalculated with this mass-dependence excluded. The tabulated sensitivity factors of Hamilton and Minski[9] and Konishi[12] are the literature values recalculated for indium as standard ($R_{In} \equiv 1$), those of Conzemius and Svec[13] are referred to lanthanum ($R_{La} \equiv 0.19$).

A similar correspondence between Hamilton's data and those obtained with the JEOL equipment was observed for relative sensitivity factors in steel matrices.[11] The low sensitivity factor for Hg is probably due to loss by volatilization during sparking.

Relative sensitivity factors for doubly-charged ions

The determination of elemental concentrations in the electrodes through the line intensities of only the singly-charged ions is possible if the fraction of multiply-charged and molecular ions of the element remains constant over all analyses. If these ratios vary irreproducibly, the sum of all possible ions of an isotope should be used for the concentration calculation.

Considering the satisfactory precision obtained in the determination of sensitivity factors for singly-charged ions, a reproducible distribution over the different ionization forms may be expected when the sparking conditions are kept constant. Nevertheless, the determination of elemental concentrations through the doubly-charged ions can be useful to account for interferences, or when all singly-charged ions suffer from interference, or for additional confirmation of the qualitative analysis. Table 3 lists the sensitivity factors for doubly-charged ions, again relative to In^+ as an internal standard. The ratio of doubly- to singly-charged ions is also tabulated. These sensitivity factors are subject to all physical and chemical influences and no prior corrections were made for ion-energy differences or energy-dependence of the plate sensitivity. Unfortunately no literature data are available for comparison.

Molecular ions

With the present sample preparation metal-molecular ions are rarely observed. Only in the case of barium carbides could some data be obtained (Table 4). Van Puymbroeck[14] has also observed the increased tendency of barium and the lanthanides (relative to

Table 3. Relative sensitivity factors for doubly-charged ions (relative to In^+)

Element	Relative sensitivity factor for M^{2+}	Ratio of relative sensitivity factors for M^{2+} and M^+, in %
V	0.06 ± 0.02	15
Co	0.18 ± 0.08	34
Ni	0.19 ± 0.10	32
Cu	0.22 ± 0.11	38
As	0.13 ± 0.03	36
Rb	0.14 ± 0.10	6
Y	0.11 ± 0.02	50
Pd	0.10 ± 0.11	16
Ag	0.38 ± 0.11	35
In	0.38 ± 0.07	38
Sb	0.16 ± 0.03	65
Ba	0.17 ± 0.07	50
La	0.11 ± 0.06	53
W	0.05 ± 0.02	34
Re	0.03 ± 0.01	14
Au	0.08 ± 0.04	24
Pb	0.10 ± 0.02	48
Bi	0.10 ± 0.02	56
Sm	0.13 ± 0.03	30
Eu	0.11 ± 0.05	40
Tb	0.07 ± 0.01	35
Ho	0.09 ± 0.04	41
Er	0.05 ± 0.02	23
Tm	0.09 ± 0.02	
Lu	0.05 ± 0.04	30
U	0.05 ± 0.01	45

Table 4. Relative abundance of barium carbide ion mass lines in the spectrum

Ion	Ba^+	BaC_1^+	BaC_2^+	BaC_3^+	BaC_4^+	BaC_5^+	BaC_6^+
Relative abundance in %	100	0.21	2.0	0.20	0.32	0.03	0.08

other metals) to form metal carbide ions, with a higher occurrence of ions with an even number of carbon atoms.

The graphite matrix itself produces a complex spectrum of molecular ions, the so-called "C-clusters". The abundance of the cluster ions, relative to the sum of all cluster ions, is represented in Fig. 1. The mean precision of the data is around 29%. The C-clusters appear to be much less abundant when salts, metal oxides (geological samples) or other carbon allotropes (fly ash) are mixed with graphite.

Accuracy and precision of the SSMS analysis of carbon electrodes

As appears from Table 2, the average error of the relative sensitivity factors is 30%. The analysis precision is defined as the standard deviation for repeated analysis of the sample. For the experimental determination of this precision two powder samples (each with 21 elements) were analysed three times, starting from the electrode preparation and finishing with a computer evaluation of the mass spectra. A mean precision of 15.7% was calculated from the 126 measured concentrations. Agreement with literature values is satisfactory (Table 5). The precision obtained with replicate analyses of the same sample (15.7%) does not differ significantly from that obtained for different samples having the same composition (16.1%). The present method of electrode preparation does not therefore add to the overall uncertainties.

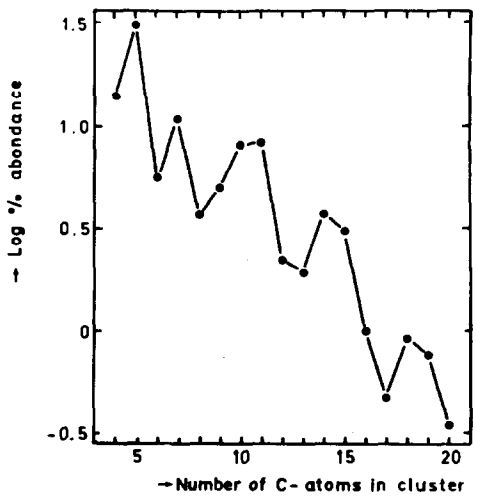

Fig. 1. Variation in abundance of carbon-cluster ions with number of carbon atoms.

Table 5. Precision of analysis of carbon matrices.

Matrix	Reference	Precision reported, %
C	This work	16
C	Burdo *et al.*[8]	17
C	Conzemius and Svec[13]	16
C	Hamilton and Minski[9]	20
C	Harrison and Clemena[16]	20–25
C-biological	Evans and Morrison[15]	17–22–31
C-geological	Jaworski and Morrison[4]	15
C-salts	Konishi[12]	7–20
C-natural water	Wahlgren *et al.*[17]	20–40

In previous work[6] the precision of the determination of isotopic abundances (which is a criterion for the evaluation of the calculation algorithm) was reported to be 6%, for isotopes with comparable abundance. When the isotopic abundances differ greatly and the mass lines occur in different regions of the photoplate, this precision becomes about 10%, as a result of imprecision in total ion monitoring and because fewer points are available in the linear part of the calibration curve for both isotopes.

The square of the difference between the precision of replicate analyses of the same sample and that of the isotopic abundance measurement is a measure of the uncertainty contributed by variations in instrumental settings and photoplate characteristics. It amounts to 12%.

The detection limit of SSMS analysis is a function of the total exposure on the photoplate. With the same exposure, the detection limit differs from plate to plate and is dependent on the elemental relative sensitivity factor, isotopic abundances and background. With a maximum exposure of 100–150 nC, the detection limit is typically 0.5–0.1 ppM* in the graphite electrodes. Since the mass line of an isotope must be measured for several different exposures in order to obtain a precise analysis, the exposure times must be increased to obtain a decrease in detection limit. The analysis time will consequently increase significantly for only a slight improvement in sensitivity.

* ppM = parts per milliard (10^9).

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REACTION-RATE METHOD FOR THE DETERMINATION OF PHOSPHORUS IN AGRICULTURAL PRODUCTS

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Summary—A new automated reaction-rate method for the quantitative determination of phosphorus in grains and feeds is presented. The chemical methodology has been investigated, resulting in a high analytical throughput with precise, accurate results. The phosphomolybdenum blue reaction is used for the reaction-rate determination. After digestion of the samples by the official AOAC block digestion procedure, automated instrumentation is used for precise and rapid combination of the reactants and transfer of the mixed solution to an automated spectrophotometer. The rate of formation of the product during 5 sec is automatically determined and compared with rates obtained for phosphorus standards to determine the phosphorus content of the sample. Relative standard deviations of about 0.3% are obtained and results for determinations of phosphorus in grains and feeds are accurate as indicated by comparison with the average obtained by all laboratories participating in the AAFCO check sample programme.

The determination of phosphorus in a variety of samples such as grains, feeds and fertilizers is of analytical importance. Phosphorus is one of the essential nutrients needed for various cellular processes in plants and performs functions in plant metabolism, structure and reproduction that cannot be performed by any other element.[1] Recognition of the importance of phosphorus has prompted the development of new methods for the determination of the phosphorus content of grains and feeds[2] and the available phosphorus in fertilizers.[3,4] Most of the existing methods use the formation of a molybdophosphoric acid complex which is monitored spectrometrically at wavelengths near 400 nm. This method is the official procedure reported by the Association of Official Analytical Chemists for the determination of phosphorus in fertilizers and grain and feed samples.[5,6] A disadvantage of the existing methods is that they employ equilibrium methods which can result in low sample throughout and can be subject to interfering side-reactions or matrix blanks.[7] A solution to the problems presented by the equilibrium methods for phosphorus is to use a reaction-rate method. Since only the early part of the reaction need be monitored in a reaction-rate method, the problem of low sample throughput caused by the delay for the reaction to come to equilibrium is avoided. Also, a reaction-rate method monitors relative absorbance changes rather than absolute absorbance as in the equilibrium methods and it is therefore not significantly affected by slightly turbid samples or background absorbance.

A reaction-rate method for the determination of phosphorus in serum samples was reported by Crouch and Malmstadt[8] in which the rate of reduction of the molybdophosphoric acid with ascorbic acid (followed by monitoring at 650 nm for 30–40 sec the formation of phosphomolybdenum blue) was used to determine the phosphorus content of the sample. As a result of the good precision and accuracy and short measurement times reported for this procedure, the reaction was investigated for use in a reaction-rate procedure for the determination of phosphorus in grain and feed samples. The procedure presented in this paper uses an early part of the phosphomolybdenum blue reaction heretofore not investigated for quantitative measurement of phosphorus. The time-saving in reaction-rate methods[7] provides a significant decrease in the measurement time and gives high throughput of samples. The results obtained by the new reaction-rate procedure are compared with those obtained the official AOAC spectrometric method for AAFCO check grain and feed samples, and good correlation is shown to exist between them.

EXPERIMENTAL

Apparatus

The pipetter/diluter for the subsampling and mixing of the diluted digest mixture and the ascorbic acid reagent is the module described by Malmstadt *et al.*[9] The module provides automatic manipulation of the reactants in a precise and accurate manner and automatic transfer of the mixed solutions to the spectrophotometer sample turntable. Fractions are taken automatically from the prepared samples and mixed with the molybdenum reagent and the mixed solutions are transferred to the observation cell of the spectrophotometer by means of a stopped-flow module.[10] The stopped-flow module is incorporated into an automatic spectrophotometer[11] controlled by associated electronics and a PDP8/F computer with 12K of memory and dual DEC tapes (Digital Equipment Corporation, Maynard, Mass. 01754).

Reagents

A 100-ppm phosphorus standard was prepared with 0.4393 g of dipotassium hydrogen phosphate, primary standard (Fisher Scientific Co., Pittsburg, PA 15219, No. P-382,

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dried for 2 hr at 105°). This was added to a 1-litre standard flask containing a mixture of 36 g of potassium sulphate and 1.68 g of mercuric oxide (*i.e.*, 37.68 g of Mixture No. 5 from Pope Kjeldahl Mixtures, Inc., Dallas, TX 75221) so that the standard was in the same matrix as that in the official AOAC block digestion procedure used to prepare the samples.[12,13] Concentrated sulphuric acid (34.8 ml) was added to the standard so that this had the sulphuric acid concentration that would be expected when a 1.5-g sample was digested according to the official digestion procedure. A blank digest containing 36 g of potassium sulphate, 1.68 g of mercuric oxide, and 34.8 ml of concentrated sulphuric acid was prepared and appropriate volumes of the 100-ppm phosphorus standard and the blank were mixed to prepare the standards for the working curve.

The ascorbic acid reagent was prepared daily with 0.53 g of ascorbic acid and 0.656 g of sodium hydroxide dissolved in 100 ml of demineralized water. This amount of sodium hydroxide resulted in a sulphuric acid concentration of about 0.06*M* in the prepared sample and this in turn ensured an acidic matrix for the phosphomolybdenum blue reaction while ensuring that the sulphuric acid in the digest did not cause deterioration of the valves of the stopped-flow module. Potassium iodide (5 g) was added to 100 ml of the ascorbic acid reagent to eliminate a grey precipitate which otherwise formed on mixing of the ascorbic acid reagent with the diluted digest. The precipitate resulted from the mercury in the digest,[12,13] but did not form when the mercury was complexed with iodide.[14,15] A yellow precipitate first forms, but rapidly dissolves if enough potassium iodide is present in the ascorbic acid reagent, and does not interfere in the spectrometric rate determination of phosphorus at 650 nm.

The molybdenum reagent (0.05M) was prepared a day before its use to ensure equilibrium of the different forms of molybdenum in solution.[16] The molybdenum concentration was chosen so that it did not change appreciably during the measurement of the rate of formation of the phosphomolybdenum blue. Sodium molybdate dihydrate (1.209 g) was added to 100 ml of 0.1*M* sulphuric acid. All standards and reagents were stored in polyethylene bottles to prevent leaching of silicon from the volumetric glassware.

Sample preparation

The samples were digested by the official AOAC block digestion procedure[12,13] used by Hambleton[2] for phosphorus determinations in grain and feed samples. The sample (1.5 ± 0.1 g) was accurately weighed and added to a dry 250-ml volumetric digestion tube (Model 1007-021 from Tecator Inc., Boulder, CO 80301), then 9.42 g of a reagent mixture of 95.5% potassium sulphate and 4.5% mercuric oxide (Mixture No. 5 from Pope Kjeldahl Mixtures, Inc., Dallas, TX 75221) were added to each digestion tube followed by 15 ml of concentrated reagent-grade sulphuric acid. The digestion tubes were placed in a block digestor (Model BD-20 from Tecator Inc., Boulder, CO 80301) which had been preheated (about 3 hr) to 410°. The samples were digested for 45 min at 410° as in the official AOAC procedure.

After digestion of the samples, the rack of tubes was removed from the block digestor and allowed to cool for 15 min. Demineralized water was slowly added to each tube until the volume was approximately 200 ml. The diluted digest was allowed to cool to room temperature and a Teflon-coated stirring bar was used to help dissolve the precipitate formed during the cooling process. The solution was then diluted to exactly 250 ml in the volumetric digestion tubes.

Reaction-rate procedure

For determination of phosphorus by the phosphomolybdenum blue method, molybdate reacts with the phosphate to form molybdophosphoric acid which is then reduced by a suitable reducing agent such as ascorbic acid. The first procedure investigated for addition of the two reagents involved the preparation of a composite reagent of molybdenum and ascorbic acid. This reagent was then added to the phosphorus-containing sample and the formation of the product was monitored at 650 nm. This procedure gave poor reproducibility (*ca.* 5% difference), however, for duplicate determinations on the same sample. The problem was instability of the composite molybdenum–ascorbic acid reagent, indicating that such a reagent should not be employed. The procedure adopted involves the addition of the alkaline ascorbate reagent to the sample, followed by the addition of the molybdate reagent, which initiates the reaction. The pipetter/diluter is loaded with the ascorbic acid reagent and the appropriate standard or sample. Two successive 1-ml aliquots of the ascorbic acid reagent and 250-μl aliquots of the sample or standard are drawn into the two syringe barrels and the mixture is delivered into a beaker to provide the "prepared sample". Then 100 μl each of the molybdenum reagent and the prepared sample or standard are sampled by the syringes of the stopped-flow module.[10] The syringes in the module are then automatically driven forward so as to transfer the reactants through the mixing chamber and into the observation cell. The change in absorbance at 650 nm is automatically recorded during the measurement time to enable a rate curve or a working curve to be constructed or to provide quantitative concentration information for a sample. The results presented in this paper were obtained with the reactants and the instrumentation at ambient temperature in a temperature-controlled laboratory maintained at about 25°.

RESULTS AND DISCUSSION

Ascorbic acid concentration

The concentration of ascorbic acid necessary to provide maximum sensitivity was the first parameter considered in the optimization study. A 9.5-mg/250 ml phosphorus standard was prepared from oven-dried dipotassium hydrogen phosphate in a matrix corresponding to that for a digested grain or feed sample (7.8m*M* mercuric oxide, 0.21*M* potassium sulphate and 0.626*M* sulphuric acid). Fractions of the sample solution were mixed by the pipetter/diluter with four different ascorbic acid reagents (0.164*M* sodium hydroxide, 0.30*M* potassium iodide and varying concentrations of ascorbic acid). The prepared samples were then automatically subsampled and mixed by the stopped-flow module with 0.05*M* molybdate–0.1*M* sulphuric acid reagent and transferred to the observation cell of the spectrophotometer. The rate of formation of phosphomolybdenum blue (PMB) was then monitored at 650 nm for 5 sec after a 2-sec delay. The results are shown in Table 1. The data indicate that the maximum sensitivity and best precision are obtained with the 0.03*M* ascorbic acid reagent.

Sulphuric acid concentration in the molybdate reagent

The optimum concentration of sulphuric acid was determined for a molybdate concentration of 0.05*M*. This concentration of molybdate provides adequate

Table 1. Effect of ascorbic acid concentration

[Ascorbic acid] *M*	Rate* *absorbance units/sec*	RSD, %*
0.005	0.0245	0.4
0.01	0.0710	0.3
0.02	0.0816	0.2
0.03	0.0824	0.2

* Average of 5 determinations.

sensitivity and is also large enough to remain essentially constant during the reaction. The concentration of sulphuric acid in the molybdate reagent was varied between 0.01 and 0.10*M*. Higher concentrations were not used because of their harmful effects on the valves of the stopped-flow module. The reaction-rate curves (monitored at 650 nm) for the formation of PMB from a 9.5-mg/250 ml phosphorus standard mixed by the pipetter/diluter with the 0.03*M* ascorbic acid reagent are shown in Fig. 1, and indicate that the sulphuric acid concentration in the molybdate reagent should be 0.10*M*. The reproducibility (5 replicates) was 0.3%.

Delay and measurement time

The reaction-rate curve for a 12.8-mg/250 ml phosphorus standard prepared with the ascorbic acid reagent was recorded to determine the optimum delay and measurement times. The resulting curve, shown in Fig. 2, indicates that an initial product formed during the first 15 sec after mixing of the reactants. One or more other reactions then began and continued for several minutes. It is these subsequent reactions that require several minutes to reach equilibrium and result in slow procedures for equilibrium methods. The reaction that occurs 15 sec after mixing the reactants is the one monitored by Crouch and Malmstadt in their procedure in which the reaction-rate curve is recorded 10–15 sec after mixing of the reactants.[8] The initial phosphomolybdenum blue reaction was further investigated because of its potential for a more rapid and sensitive reaction-rate procedure. The reaction-rate curves for a 20 mg/250 ml phosphorus standard and a reagent blank are shown in Fig. 3. The curve indicates that there is an induction period during the first few seconds after mixing of the reactants, presumably due to the formation of the molybdophosphoric acid precursor of the phosphomolybdenum blue. It can be seen from the blank in Fig. 3 that there is no significant background effect which contributes to the measured rate for the sample. The effect of varying the delay and measurement time on reproducibility of the determination is shown in Table 2. Based on these results, a measurement time of 5 sec after a 2-sec delay was selected.

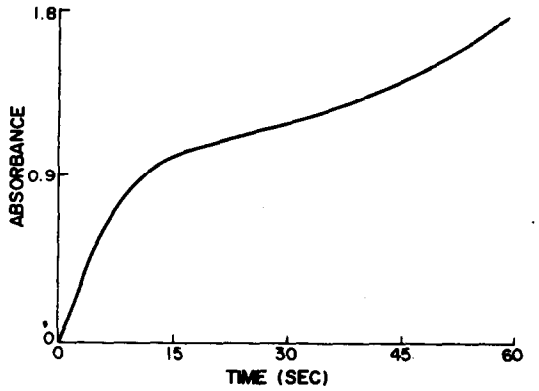

Fig. 2. Reaction-rate curve for a phosphorus standard.

Digest matrix conditions

In this study, it was noted that during the digestion of 1.5 g of grain or feed samples, the acid loss from boiling and digestion ranged from 42–52% of the original acid added to the sample. The effect of this on the reaction-rate method for phosphorus was examined. A series of 2.5 mg/250 ml phosphorus standards was prepared in the potassium sulphate–mercuric oxide matrix with sulphuric acid concentration 0.626–0.518*M* to simulate the range of acid present in digested samples. Fractions of the samples were

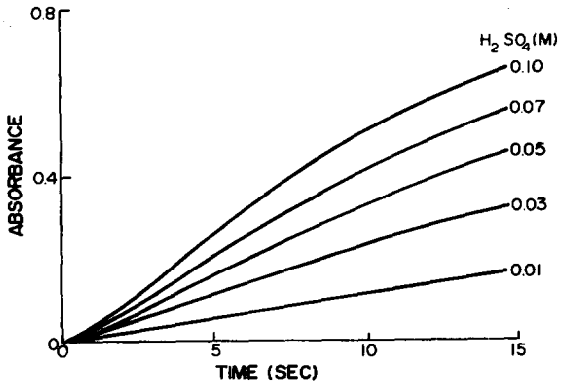

Fig. 1. Reaction-rate curves for different H_2SO_4 concentrations in the Mo reagent.

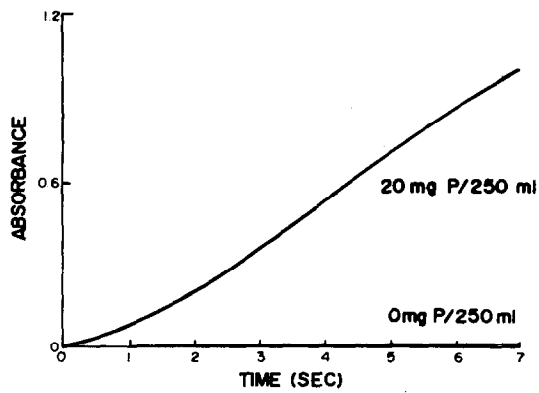

Fig. 3. Reaction-rate curves for 20 mg/250 ml phosphorus standard and a blank.

Table 2. Choice of delay and measurement time

Delay, *sec*	Measurement, *sec*	Rate*, *absorbance units/sec*	RSD, %*
2	3	0.0721	0.4
3	3	0.0744	0.3
2	5	0.0732	0.2
3	5	0.0730	0.2

* Average of 5 determinations.

Table 3. Effect of acid loss during digestion

Acid loss, %	Rate,* *absorbance units/sec*
42	0.0221
44	0.0221
46	0.0223
48	0.0223
50	0.0222
52	0.0223
	Mean 0.0222
	RSD 0.4%

* Average of 4 determinations.

mixed with the ascorbic acid reagent by the pipetter/diluter. The stopped-flow module then sequentially subsampled and mixed the samples with the molybdate reagent and transferred the solution to the observation cell of the spectrophotometer. The absorbance change at 650 nm was monitored for 5 sec after a 2-sec delay. The results in Table 3 indicate that within this range, the reaction-rate method is not significantly influenced by variations in the sulphuric acid concentration in the digested sample.

The digestion procedure used[12,13] specifies that use of 0.42 g of mercuric oxide in the digestion procedure and suggests the possible use of a calibrated scoop for measuring it out. Various amounts of mercuric oxide were added to standard samples which were then digested, cooled, and diluted and analysed as in the procedure. As indicated by the data in Table 4, fairly large variations in the amount of mercury present in digested samples during analysis have no effect on the reaction-rate method.

Reaction-rate results

The optimum conditions determined from the characterization studies were used to evaluate the precision and accuracy of the method. The reproducibility

Table 4. Effect of amount of mercuric oxide

HgO, *mg/250 ml*	Rate, *absorbance units/sec*
350	0.1107
400	0.1106
450	0.1107
500	0.1109
	Mean 0.1107
	RSD 0.1%

* Mean of 5 determinations.

Table 5. Precision study for optimized conditions

	Ten separate samples*	Ten detns. from same soln.
Mean P, %	0.598	0.602
Std. devn., P, %	0.0045	0.0018
RSD, %	0.8	0.3

* AAFCO Check Sample Number 7726. Official AOAC result 0.598 ± 0.042% (grand average from 23 labs., reported 16 August 1977).

Table 6. Typical working curve

P, *mg/250 ml*	Rate, *absorbance units/sec**	RSD, %	Normalized rate†
2.52	0.0225	0.3	0.00892
6.00	0.0525	0.2	0.00875
9.50	0.0817	0.2	0.00860
12.78	0.1117	0.3	0.00874
16.49	0.1419	0.2	0.00860
19.92	0.1727	0.1	0.00868

* Average of 5 determinations.
† Referred to 1 mg/250 ml.

with which the samples were digested and the phosphorus content of the digested sample was determined is shown in Table 5. The results demonstrate the good precision (relative standard deviation 0.3%) obtained for multiple determinations on a single sample prepared by the pipetter/diluter.

The reproducibility for independent digestions was not quite so good, the complete analytical procedure having a relative standard deviation of 0.8%.

The results obtained for a working curve constructed in a little over 4 min during a typical run are shown in Table 6 and demonstrate the excellent precision and linearity obtained for the standards.

To evaluate the accuracy of the method, a series of samples analysed by several laboratories by an official AOAC method[6] was analysed. The results are given in Table 7 and show good agreement.

Table 7. Comparison of stopped-flow method with official AOAC method[5]

Sample	Stopped-flow method P, %*	Official method[17] P, %†	RSD, %
7726	0.600	0.598	0.3
Swine Ration	±0.002§*	±0.042§*	
7727	1.027	1.037	0.6
Expanded Pet Food	±0.006	±0.115	
7729	0.588	0.580	0.2
Pig Feed	±0.001	±0.025	
7730	0.571	0.560	0.7
Broiler Finisher	±0.004	±0.026	

* Results for 3 separate digestions with 4 determinations performed on each digestion.
† Values reported in AAFCO Check Sample Programme by 20 laboratories, during 1977.
§ Standard deviation.

The method reported here provides rapid, precise and accurate determination of phosphorus in grain and feed samples and has the distinct advantages of high sample throughput and utilization of a relatively simple automated system.

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DETERMINATION OF SELENIUM IN SOILS AND PLANTS BY DIFFERENTIAL PULSE CATHODIC-STRIPPING VOLTAMMETRY*

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Summary—A method is described for the determination of selenium by differential pulse cathodic-stripping voltammetry (DPCSV) at a hanging mercury-drop electrode. The dried sample is burnt in an oxygen flask and the selenium absorbed in a persulphate–sulphuric acid mixture. The solution is analysed by DPCSV following treatment with hydrochloric acid to destroy excess of persulphate and to reduce the Se(VI) to Se(IV). Results are given for two soils and a series of plant materials and compared with those obtained by fluorimetric analysis by means of the 2,3-diaminonaphthalene piazselenol complex.

Considerable effort has been directed towards measuring selenium in soils and plant materials since the element was found to be essential for healthy animal development.[1] A biochemical role of selenium has been described by Rotruck *et al.*[2] in which the element is incorporated into the enzyme glutathione perioxidase, preventing oxidative degradation of red blood cells. In N. Scotland muscular dystrophy encountered in grazing stock is due to selenium deficiency in natural forage, associated with poor availability from the soil;[3] Blaxter[4] has shown the dramatic loss of production associated with sheep fed on a selenium-deficient diet. Sensitive analytical techniques are, therefore, necessary to determine the selenium content of soils, plants and biological samples.

Selenium is usually determined by fluorimetry after complexation with diaminonaphthalene or diaminobenzidine,[5] but neutron-activation analysis,[6] gas chromatography,[7] spectroscopic[8] and electrochemical methods[9,10] have also been used. In order to obtain greater reproducibility and lower detection limits, various separation and preconcentration techniques have been investigated, *e.g.*, ion-exchange,[11] solvent extraction,[12] precipitation,[13] complexation,[14] distillation[15] and hydride generation procedures.[16]

The polarographic behaviour of selenium(IV) was first reported by Schwaer and Suchy[17] who observed that in hydrochloric acid medium there were three waves, arising from the reduction to Se^{2+}, Se and Se^{2-}, although in dilute solutions the first two waves were indistinguishable. Christian, Knoblock and Purdy[18] found the half-wave potentials of the two waves in 0.1*M* hydrochloric acid medium were −0.01 V and −0.54 V *vs.* the saturated calomel electrode, corresponding to the following reactions.

At −0.01 V:	$Se(IV) + 6e + 2H^+ \rightarrow H_2Se$
	$H_2Se + Hg \rightarrow HgSe + 2H^+ + 2e$ depolarization
Net reaction	$Se(IV) + 4e + Hg \rightarrow HgSe$
At −0.54 V:	$HgSe + 2H^+ + 2e \rightarrow H_2Se + Hg$

Vadja[19] examined the reactions of Se(IV) at a hanging mercury drop electrode and observed an elongated wave and a well-defined peak corresponding to the reductions described above. However, in the presence of halide ions a superimposed sharp peak appeared on the wave, indicating the adsorption of a hexahaloselenium complex onto the mercury drop. The Se(IV) thus accumulated could be removed by cathodic stripping and Vadja showed that the peak heights observed at −0.01 and −0.54 V were proportional to the selenium concentration.

This paper describes a method for the determination of selenium in soils and plants by differential pulse cathodic stripping voltammetry (DPCSV) at a hanging mercury-drop electrode. Oxygen-flask digestion of the sample as described by Lane[20] and modified by Mitchell and Ure[21,22] is followed by treatment with hydrochloric acid to reduce Se(VI) to Se(IV). The voltammogram is then recorded following standard addition of 0.02 ppm Se and the selenium concen-

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tration determined by measurement of the stripping peak at −0.54 V.

EXPERIMENTAL

Apparatus and solutions

Combustions were performed in a 5-litre Pyrex round-bottomed flask with a ground-glass stopper to which a glass rod and silica sample boat were attached. Voltammograms were recorded with a Princeton Applied Research Model PAR 174A Polarographic Analyzer and a hanging mercury-drop electrode Model PAR 9323. The PAR 174A was connected to a Houston Instruments Omnigraphic 2000 X-Y recorder. All chemicals used were analytical-reagent grade and Se(IV) solutions were made up by dissolving sodium selenite in water. Distilled water which had been passed through a mixed-bed ion-exchange resin was used throughout, and the Se(IV) solutions were standardized by gravimetric analysis.[23]

Procedure

Air-dried soil (1 g, ground to pass 150-μm mesh) was mixed with 0.5 g of cellulose powder and pelleted in a die under the minimum pressure necessary. Dried, milled plant material (1 g) was found to burn satisfactorily without the addition of cellulose and could be pelleted directly. Saturated potassium persulphate solution (25 ml) was added to the 5-litre flask and 10 ml of concentrated sulphuric acid were carefully poured down the inside of the vessel. The reagents were mixed by agitating the flask, which was then filled with oxygen, stoppered and placed behind a Perspex safety shield. The sample pellets were wrapped in filter paper (with a tag to act as a fuse) and placed in the silica boat, the flask stopper was removed, the fuse ignited and the holder carefully inserted into the flask. In order to achieve a good seal the ground-glass union was wetted prior to insertion of the holder. When combustion had ceased, the flask was allowed to cool naturally for a few minutes and then further cooled in running water. The sample holder and ash were withdrawn and a magnetic stirring bar placed in the flask, which was then stoppered and the collecting solution was stirred for 15 min. Finally, the absorption solution and washings were transferred to a beaker, 10 ml of concentrated hydrochloric acid were added and the mixture was gently heated on a low-temperature hot-plate for 30 min to reduce the volume and convert Se(VI) into Se(IV); the volume was then made up to 50 ml in a standard flask. Blanks and standards were prepared in a similar manner by adding Se(IV) standard solutions by micropipette onto cellulose pellets, and burning these in the flask.

Aliquots of the solutions (10 ml) were taken and 5 ml of conc. ammonia solution added dropwise with stirring. The pH, measured with a glass electrode, was then adjusted with dilute hydrochloric acid to 3.5 (±0.2) and the solution made up to 20 ml with demineralized distilled water. A 5-ml aliquot of this solution was pipetted into the polarographic cell and deoxygenated by passage of nitrogen through it for 5 min. Concentrated hydrochloric acid (50 μl) and a fixed quantity of selenium solution (corresponding to 0.02 ppm) were added and the nitrogen flow was directed above the solution. The stripping voltammogram was then recorded under the following conditions.

HMDE: 3 div/drop
Initial potential: −0.05 V
Pulse frequency: 2 Hz
Scan-rate: 2 mV/sec
Scan direction: negative
Modulation amplitude: 25 mV
Deposition time: 3 min (stirred) and 30 sec (quiescent)

The peak current at −0.54 V was measured and a calibration curve constructed from the results for the standards. Supplementation of all solutions by 0.02 ppm Se immediately before the voltammograms were recorded ensured that measurements were made on the linear region of the calibration curve. The selenium content in the sample solutions could then be directly determined from the calibration curve. The results were compared with those obtained by fluorimetry by Olson's method[5] in which the piazselenol complex was formed by reaction with 2,3-diaminonaphthalene.

RESULTS AND DISCUSSION

The selenium concentrations obtained by DPCSV and fluorimetric analysis of soil and plant samples are given in Table 1. Linear regression analysis of these data gave a correlation coefficient of 0.98, and indicated that the electrochemical and spectroscopic figures are in reasonable agreement above 0.1 ppm.

An examination of the results in Table 1 shows that at low selenium concentrations there is a definite positive bias in the electrochemical results when these are compared with the spectrofluorimetric results. This divergence is compounded by multiplication of the electrochemically determined concentration by the dilution factor of 10 or 25. It should be noted here that good agreement has been obtained between the spectroscopic and electrochemical procedures for pure solutions containing *ca.* 0.001 ppm Se.

Oxygen-flask combustion

Although more time-consuming than wet digestion techniques, the oxygen-flask combustion was preferred because it eliminates the interferences in the DPCSV method that are observed if wet digestion is used and because of the potential hazards associated with the use of perchloric acid in the laboratory. At the flask-combustion temperature of 100–1200° the selenium would be converted into the volatile dioxide, and neutral or basic solutions might be expected to be the best collecting agents. The efficiencies of 0.1, 0.5 and 1.0*M* sodium hydroxide as absorption solutions were investigated, but recoveries obtained were only 50% of the theoretical values. Digestions with different Se(IV) standards gave consistent recoveries which were independent of the initial amounts of selenium, and combustions in 1-litre flasks produced the same results, indicating that the loss is not attributable to adsorption on the walls of the vessel. It was found that Se(VI) standards burnt in the flask gave quantitative recoveries when water was used as the collecting agent. This suggested that reduction of Se(IV) to the element might account for the low recoveries.

Radiotracer studies were carried out with ^{75}Se-labelled methionine solutions. Six samples were burnt in the flask after sorption onto cellulose tablets and recoveries were determined for water and persulphate–sulphuric acid as absorption media.

Table 1. Selenium concentrations determined by DPCSV and fluorimetric analysis of soil and plant materials

Sample		Description	Conc. found by DPCSV, *ppm*	Conc. found by fluorimetry, *ppm*
Soil	7131	(Logie Newton) Foudland Association	0.42	0.39
	7136	(Ashfield) Glenalmond Association	0.38	0.31
Plant	1	Ryegrass	0.99	0.94
	2	Ryegrass	0.46	0.61
	3	Ryegrass	1.61	1.27
	4	Ryegrass	0.25	0.24
	5	Ryegrass	0.02	0.01
	6	Ryegrass	0.58	0.65
	7	Ryegrass	3.34	3.44
	8	Ryegrass	0.31	0.18
	9	Ryegrass	2.31	2.85
	10	Ryegrass	0.25	0.46
	11	Ryegrass	1.01	0.90
	12	Ryegrass	0.10	0.01
	13	Mixed Herbage	0.24	0.21
	14	Mixed Herbage	1.11	1.26
	15	Mixed Herbage	0.85	0.61
	16	Mixed Herbage	0.21	0.04
	17	Mixed Herbage	0.60	0.36
	18	Clover	0.13	0.01

Table 2. Recoveries of selenium from methionine combusted in an oxygen flask; H_2O and $S_2O_8^{2-}/H_2SO_4$ as absorbents

Water	77%	67%	70%	Mean 71%
Persulphate/sulphuric acid	100%	100%	95%	Mean 98%

Interferences

Consideration of the electrode reactions described in the introduction reveals that many interferences may be encountered in the electro-determination of selenium. The presence of metal ions such as copper(II), lead and iron(III) in the analyte leads to the precipitation of selenides on reduction of Se(IV) to hydrogen selenide. Consequently the peak height at −0.54 V diminishes when interfering metal ions are present. The magnitude of the peak suppression produced by copper is shown in Fig. 1.

Metal ion interference was not encountered when the oxygen-flask combustion was used, as the volatile selenium was separated from the ash. The removal of interfering ions would be necessary, however, following wet digestion methods, so some experiments were carried out to investigate the separation of copper from selenium. A solution of dithizone in carbon tetrachloride was used to extract the copper, but this reagent also reacts with selenium,[24] thus preventing an effective separation. Both Zeokarb 225 and Amberlite IR 120(H) cation-exchange resins were found to separate copper in the pH range 3.5–4.5 with no retention of selenite, and it was, therefore, possible to remove copper quantitatively from a solution containing 0.02 ppm Se(IV) and 60 ppm Cu(II).

Optimization of control parameters

Vadja[19] reported that Se(IV) in the presence of halide ions is adsorbed onto the mercury-drop elec-

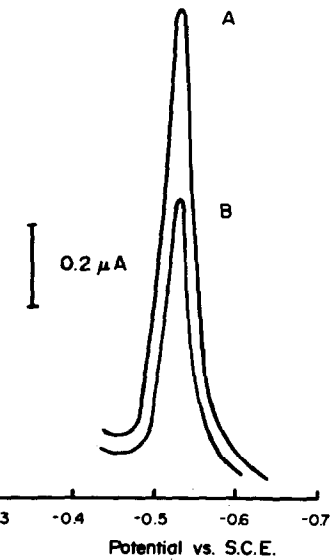

Fig. 1. Effect of presence of Cu(II) on the voltammogram for selenium(IV): (A) Voltammogram for 0.02 ppm Se(IV); (B) Voltammogram for 0.02 ppm Se(IV) + 0.02 ppm Cu(II).

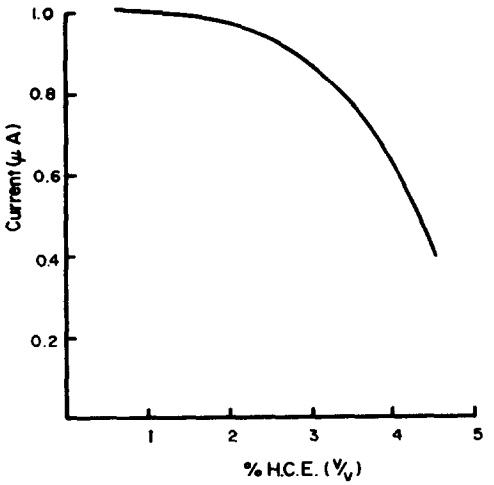

Fig. 2. Effect of acid concentration on the magnitude of the stripping current for 0.02 ppm Sc(IV) solution at −0.54 V.

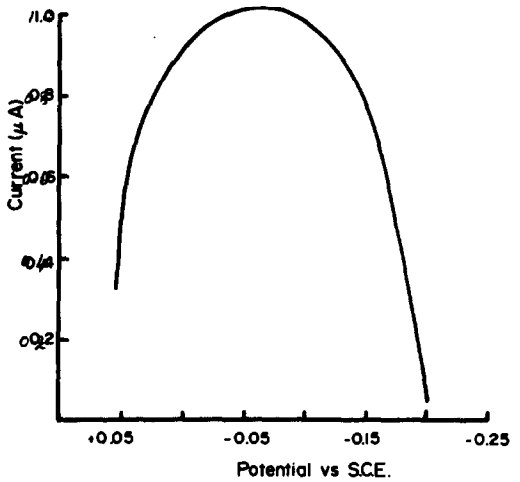

Fig. 3. Effect of deposition potential on the magnitude of the stripping current for 0.02 ppm Se(IV) solution at −0.54 V.

trode as the hexahaloselenium complex. No indication was given of the effect that halide ion concentration had on the stripping current, although changes in peak potential are well documented. It was found that increasing the acid concentration above ~0.1*M* lowered the peak height at −0.54 V, as shown in Fig. 2.

The sensitivity of inverse voltammetry can be improved by increasing the deposition time prior to stripping, but other reactions such as diffusion of the accumulated species into the mercury drop become more troublesome. It was found that increasing the deposition time from 2 min (stirred) and 30 sec (quiescent) to 3 min (stirred) and 30 sec (quiescent) produced a small rise in the stripping current, but at longer deposition times the background increased so markedly that peak-height measurement became inaccurate.

The peak current was measured after accumulation for 3½ min at initial potentials of +0.05, 0.0, −0.05, −0.10, −0.15 and −0.20 V *vs.* SCE. Figure 3 shows that the current increased as the potential was changed from +0.05 to 0.0 V, but thereafter remained almost constant until a potential of −0.15 V was reached, whereupon the peak height diminished. Thus −0.05 V was chosen as the optimum deposition potential for differential pulse cathodic stripping of selenium.

Increasing the modulation amplitude from 25 to 50 mV did not increase the stripping current and the peak resolution was found to deteriorate slightly. Voltammograms were recorded at pulse frequencies of 0.5, 1.0 and 2.0 Hz, but this parameter also appeared to have little effect on the magnitude of the stripping current.

Conclusions

Selenium can be determined in soils and plant materials by differential pulse cathodic-stripping voltammetry at a hanging mercury-drop electrode. Quantitative recoveries were obtained from oxygen-flask combustions when an oxidizing solution such as persulphate–sulphuric acid was used to collect the selenium. A separation procedure prior to polarographic analysis was unnecessary since the interfering metals were retained in the ash. Wet digestion techniques would require the removal of metals which precipitate as selenides in acidic media.

Results obtained by DPCSV show reasonable agreement with those of fluorimetric analyses for selenium above 0.1 ppm in soils and plants and the detection limit of 0.005 μg/g is similar for both methods. The electrochemical method is quicker than the fluorimetric technique and involves fewer operations. Because there is no way of knowing the true selenium content of the samples used, it is impossible to say which method gives the better results.

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STUDY ON SEMI-GLYCINECRESOL RED COMPLEXES WITH BIVALENT METAL IONS

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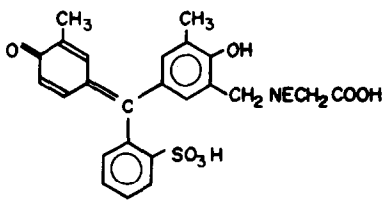
Summary—Semi-Glycinecresol Red (SGCR or H_3SGCR) was purified by means of chromatography on cellulose and by cation-exchange. A potentiometric, spectrophotometric and ESR study on the complex formation equilibria of several bivalent metal ions with SGCR was performed. The acid–base and metal–ligand stoichiometries were determined, and the formation constants, λ_{max} and absorptivities of the visible-region absorption spectra of the corresponding proton and metal complexes were determined. The copper complexes were examined by ESR spectroscopy. Each metal ion was found to form the 1:1 and 1:2 (metal:ligand) complex species, $MSGCR^-$ and $M(SGCR)_2^{4-}$, in alkaline solution. However, only Cu(II) was found to form the protonated complexes, CuHSGCR and $Cu(HSGCR)_2^{2-}$, in weakly acidic media. SGCR is suitable as an indicator for Cu(II) in a weakly acidic solution and for Cu(II), Zn(II) and Pb(II) in alkaline solution

Semi-Glycinecresol Red (SGCR or H_3SGCR), 3-(*N*-carboxymethylaminomethyl-*o*-cresolsulphonephthalein, which is shown in formula (I), is thought to be produced in the course of synthesis of Glycinecresol Red, 3,3′-bis(*N*-carboxymethylaminomethyl)-*o*-cresolsulphonephthalein. SGCR has not hitherto been purified, hence its physico-chemical properties such as the stoichiometry stabilities and visible-region absorption spectra of its complexes, which are important factors in its analytical application as an indicator, are not known in detail.

In the present work, SGCR was synthesized and purified by means of chromatography on cellulose and by cation-exchange, and the value of SGCR as an indicator for titration of several bivalent metal ions was investigated potentiometrically, spectrophotometrically and by ESR spectrometry.



(I) SGCR

EXPERIMENTAL

Reagents

SGCR. SGCR was synthesized[1] and purified by means of cellulose column chromatography[2] with n-butanol saturated with 5% acetic acid solution and by batchwise ion-exchange.[3] The purity of the SGCR was established by elemental analysis, potentiometric titration, paper chromatography and absorption spectra (found: C, 58.8%; H, 5.1%; N, 2.8%; calculated for $C_{24}H_{23}O_7NS \cdot H_2O$: C, 59.12%; H, 5.17%; N, 2.87%).

Stock solutions of metal ions, 0.01 M. Prepared by dissolving analytical-reagent grade metal nitrates in pure water, and standardized with EDTA. The solutions were diluted to the desired concentration with pure water.

Apparatus

Visible spectrophotometry and pH-titrations were performed as described previously.[3] Concentrations of SGCR used were $1.0 \times 10^{-3}M$ for pH-titration and $1.0 \times 10^{-5}M$ for visible-region spectral measurements, and the concentrations of the metal ions were varied according to the desired mole ratio.

ESR. ESR spectra of the Cu(II) complexes were recorded with a JEOL JES-ME X-band spectrometer with 100-kHz modulation and the field was calibrated with Mn^{2+}-doped magnesium oxide powder. The measurements were carried out in solution at 298 K and in frozen media at 77 K. The quartz sample tubes were 1 and 4 mm in internal diameter for the measurements at 298 and 77 K respectively. The solvents were water at 298 K, and water–ethylene glycol mixture (1:1 v/v) at 77 K. The pH was adjusted with sodium hydroxide and perchloric acid. The concentration of Cu(II) was $5.0 \times 10^{-3}M$ and that of SGCR was varied according to the mole ratio desired.

RESULTS AND DISCUSSION

Acid dissociation equilibrium and optical constants of SGCR

These were determined as described previously[2] and the values are summarized in Tables 1 and 2, respectively. Consideration of the acid formation and

Table 1. Acid formation constants of SGCR at 25°C and $\mu = 0.1$ (KNO_3)

$\log k_1$	$\log k_2$	$\log k_3$	$\log k_4$	$\log k_5$
10.07	7.44*	2.47*	−0.27	−1.76

* Measured by pH-titration, the rest by spectrophotometry at room temperature.

optical constants suggests that k_1, k_2, k_3, k_4 and k_5 correspond to protonation of the imino, phenolic, carboxylic, quinone and sulphonic groups respectively.[2]

Complex formation equilibria

Cu(II) complexes. The titration curves will be referred to as the "1/1" and "1/2" curves, corresponding to titrations of SGCR when the mole ratio of Cu(II): SGCR is 1:1 and 1:2 respectively. The 1/1 curve (Fig. 1) shows two well-defined inflection points at $a = 2$ and $a = 3$ (where a is number of moles of base added per mole of SGCR), indicating the following equilibria involved in the solution.

$a = 0$–2:

$$Cu^{2+} + H_3SGCR \rightleftharpoons CuHSGCR + 2H^+$$

$a = 2$–3:

$$CuHSGCR \rightleftharpoons CuSGCR^- + H^+$$

The 1/2 curve in Fig. 2 shows three inflections at $m = 3$, 4 and 6 (where m is number of moles of base added per mole of metal ion), although these inflections are not so well-defined as those of the 1/1 curve. The buffer region between $m = 3$ and 4 was at almost the same pH as that between $a = 2$ and 3 for the 1/1 curve. Therefore, CuHSGCR, which is formed below $m = 3$, may dissociate a proton. The pH of the buffer region between $m = 4$ and 6 was almost identical to that between $a = 1$ and 2, in which a

Table 2. Wavelengths of maximum absorbance and molar absorptivities of ligand and complex species for SGCR at room temperature and $\mu = 0.1$ (KNO_3)

Species	λ_{max}, nm	Absorptivity, 10^4 $l.mole^{-1}.cm^{-1}$
L^{3-}	582	6.76
HL^{2-}	578	6.42
H_2L^-	442	2.69
H_3L	442	2.69
H_4L^+	518	4.16
H_5L^{2+}	518	6.78
MnL^-	575	4.38
CoL^-	577	4.45
NiL^-	580	5.77
CuL^-	538	3.45
$CuHL$	475	2.41
ZnL^-	540	3.75
CdL^-	574	5.31
PbL^-	523	2.75
$Ni(OH)L^{2-}$	550	4.32
	587	4.87
$Pb(OH)L^{2-}$	577	4.72

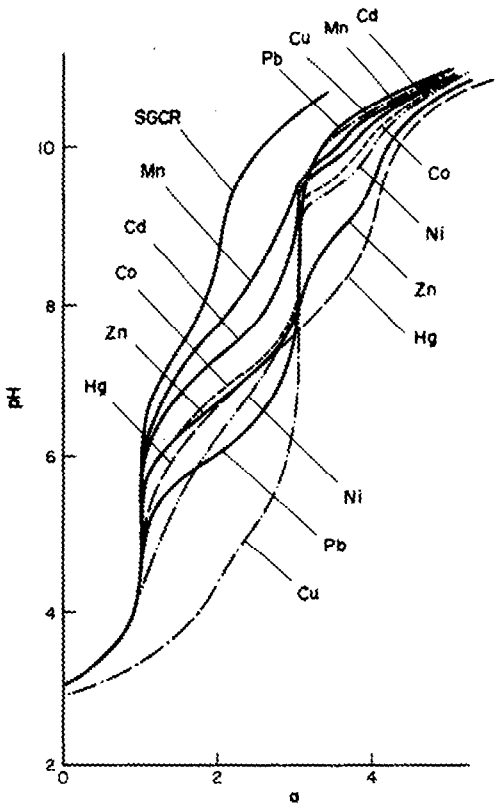


Fig. 1. Titration curves of 1×10^{-3} M SGCR solutions containing 1:1 molar ratio of metal ion to SGCR, at 25°C and $\mu = 0.1$ (KNO_3). a = number of moles of base added per mole of SGCR.

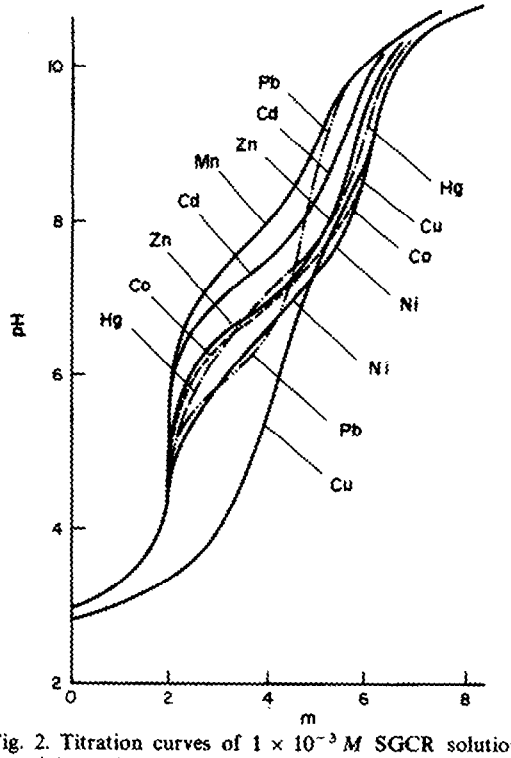


Fig. 2. Titration curves of 1×10^{-3} M SGCR solutions containing 1:2 mole ratio of metal ion to SGCR, at 25°C and $\mu = 0.1$ (KNO_3). m = number of moles of base added per mole of metal ion.

free H_2SGCR^- may dissociate a proton and then the free $HSGCR^{2-}$ may react with $CuSGCR^-$ to form the 1:2 complex species $Cu(SGCR)_2^{4-}$ (hereafter, the complexes with 1:1 and 1:2 mole ratios of metal ion to SGCR are referred to as the "1:1" and "1:2" complexes). The reactions involved in the 1/2 solution are probably as follows.

m = 0–3:

$$Cu^{2+} + H_3SGCR \rightleftharpoons CuHSGCR + 2H^+$$

$$H_3SGCR \rightleftharpoons H_2SGCR^- + H^+$$

m = 3–4:

$$CuHSGCR \rightleftharpoons CuSGCR^- + H^+$$

m = 4–6:

$$H_2SGCR^- \rightleftharpoons HSGCR^{2-} + H^+$$

$$CuSGCR^- + HSGCR^{2-} \rightleftharpoons Cu(SGCR)_2^{4-} + H^+$$

The visible absorption spectra of the 1/1 Cu(II) solution at various pH values showed the complex-formation behaviour assumed from the potentiometric titration. However, the spectra of the 1/2 solutions were very broad, indicating that many reactions were involved, and the stoichiometries of the complexes were difficult to determine from these spectra.

ESR spectra of the frozen 1/1 and 1/5 Cu(II) solutions at 77 K are shown in Fig. 3. As seen in spectra 1 and 2, at pH 4 (which corresponds to the pH-value at $a = 2$ on the 1/1 titration curve and $m = 3$ on the 1/2 titration curve) three kinds of Cu(II) species are detected, with spectra indicated by (*a*), (*b*) and (*c*) [(*b*) in spectrum 1 is the same as (*b*) in spectrum 2]. The ESR spectra will be discussed later in detail. Spectrum (*a*) is probably that of the aquated Cu(II) ion. From the pH-titration, (*b*) may be attributed to the complex species CuHSGR. The third complex, indicated by (*c*), is not detected from the pH-titrations and the visible-region absorption spectra, and is probably the 1:2 complex species $Cu(HSGCR)_2^{2-}$.

The spectra of the 1/1 and 1/5 solutions at pH 7 were also quite similar and may be attributed to the complex $CuSGCR^-$. The spectrum of the 1/1 solution at pH 10 is akin to that recorded at pH 7. The spectrum of the 1/5 solution shows the overlapping hyperfine spectra of probably two complex species, with two different A splittings, indicated by (*d*) and (*e*). The spectrum (*d*) is identical in 4 and 5 and may be attributed to the same complex species, so spectrum (*e*) is probably attributable to the complex $Cu(SGCR)_2^{4-}$. Although these protonated complexes cannot be deduced from the pH-titration curves and visible-region spectra at pH < 4 the ESR spectra show them to be formed at pH nearly down to 3.

The visible-region absorption spectra became similar to that of SGCR above pH *ca.* 11 for the 1/1 and pH *ca.* 12 for the 1/2 solutions and the ESR spectra became similar to that of the tetrahydroxocuprate ion, $Cu(OH)_4^{2-}$, above pH *ca.* 11 for the 1/1 and pH *ca.* 12.5 for the 1/5 solutions. These findings suggest that the complex species $CuSGCR^-$ and $Cu(SGCR)_2^{4-}$ may dissociate to give the free $Cu(OH)_4^{2-}$ ion and $SGCR^{3-}$. Signs of a hydroxo complex of Cu(II) and SGCR could not be detected in the visible-region and ESR spectra.

Other metal complexes. The 1/1 curves for Zn(II), Ni(II), Co(II), Cd(II) and Mn(II) have three inflection points at $a = 1$, $a = 3$ and $a = 4$ as seen in Fig. 1, and the curves between $a = 0$ and $a = 1$ are identical to the titration curve of SGCR, indicating that these metal ions do not react with SGCR at pH below 5. Further addition of base beyond a = 3–4 results in a white precipitate of the metal hydroxide, and therefore the following reactions probably occur after $a = 1$.

a = 1–3:

$$Zn^{2+} + H_2SGCR^- \rightleftharpoons ZnSGCR^- + 2H^+$$

a = 3–4:

$$ZnSGCR^- + 2H_2O \rightleftharpoons Zn(OH)_2 + HSGCR^{2-} + H^+$$

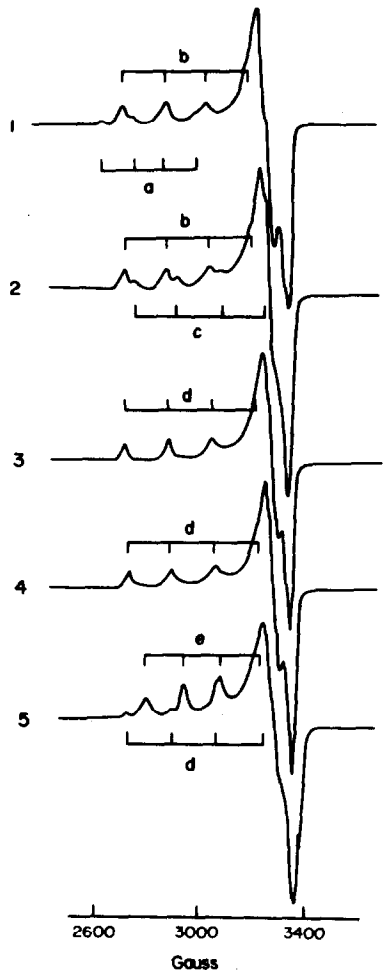


Fig. 3. First-derivative ESR spectra of the Cu(II) and SGCR solutions (at 77 K) at various pH values and mole ratios. Cu(II): 5×10^{-3} *M*. Mole ratio of Cu(II) to SGCR: *1*–1/1, *2*–1/5, *3*–1/1 and 1/5 (spectra identical), *4*–1/1, *5*–1/5. pH: *1* and *2*–4.0, *3*–7.0, *4* and *5*–10.0.

The 1/1 Pb(II) curve has two inflections at $a = 1$ and $a = 3$, and the shape of the curve between them is similar to that for Zn(II) but there is no visible inflection at $a = 4$. Thus the behaviour of Pb(II) is similar to that of Zn(II) below $a = 3$, and to that of Cu(II) above $a = 3$.

The 1/1 Hg(II) curve has a long sloping buffer region between $a = 1$ (pH 5) and $a = 4$ (pH 9), where a white precipitate is formed, and this may indicate that formation and hydrolysis of the complex overlap, production of the species $Hg(OH)_2$ and $HSGCR^-$ being complete at $a = 4$, liberating three moles of protons per mole of SGCR in this buffer region.

The 1/2 curves for Zn(II), Co(II), Ni(II) and Cd(II) have two inflections at $m = 2$ and $m = 6$. In the long buffer region in between, first the 1:1 and then the 1:2 complex species may be formed. The reactions are probably the following.

$m = 2$–6:

$$Zn^{2+} + H_2SGCR^- \rightleftharpoons ZnSGCR^- + 2H^+$$

$$H_2SGCR^- \rightleftharpoons H^+ + HSGCR^{2-}$$

$$ZnSGCR^- + HSGCR^{2-} \rightleftharpoons Zn(SGCR)_2^{4-} + H^+$$

The 1/2 Pb(III) and Mn(II) curves have two inflections at $m = 2$ and $m = 5$. The reactions involved are

$m = 2$–5:

$$Pb^{2+} + H_2SGCR^- \rightleftharpoons PbSGCR^- + 2H^+$$

$$H_2SGCR^- \rightleftharpoons HSGCR^{2-} + H^+$$

and the formation of the 1:2 complex would probably occur at higher pH after $m = 5$, the reactions perhaps being

$m > 5$:

$$HSGCR^{2-} \rightleftharpoons SGCR^{3-} + H^+$$

$$PbSGCR^- + SGCR^{3-} \rightleftharpoons Pb(SGCR)_2^{4-}$$

The 1/2 Hg(II) curve has a long buffer region between $m = 2$ and $m = 6$, and then a white precipitate appears. The reactions in the Hg(II) solution probably involve the successive formation of the 1:1 complex then and 1:2 complexes, and finally hydrolysis.

The visible-region spectra of the 1/1 and 1/2 solutions showed changes at two pH-values corresponding to those of the buffer region of the pH-titration, where the formation and the hydrolysis of the complexes $MSGCR^-$ and $M(SGCR)_2^{4-}$ occurred. In alkaline solution, the spectra of the Zn(II), Cd(II), Co(II) and Mn(II) systems showed no evidence of hydroxo complexes or direct dissociation to $M(OH)_2$ and ligand. However, the spectra for the Pb(II) and Ni(II) systems showed two reactions, indicating existence of the hydroxo complexes[4] $Pb(OH)L^{2-}$ and $Ni(OH)L^{2-}$ and their dissociation to $M(OH)_2$ (precipitated) and SGCR at pH above 12. The spectrum corresponding to $Ni(OH)L^{2-}$ had two absorption maxima at 550 and 587 nm, but that for $Pb(OH)L^{2-}$ had only one maximum.

The optical constants for the metal complexes of SGCR are summarized in Table 2; those for the 1:2 complexes were difficult to determine because the complexation reactions are so complicated.

Formation constants of the metal complexes of SGCR are listed in Table 3. They were calculated by an adaptation[4] of Bjerrum's method. The constants K_{MHL} for CuHSGCR and $K_{M(OH)L}$ for $Pb(OH)SGCR^{2-}$ and $Ni(OH)SGCR^{2-}$ were obtained graphically from the plots of log[MHL]/[ML] and log[ML]/[$M(OH)_nL$] *vs.* pH or pOH by the methods previously described.[5]

ESR spectra and parameters

The ESR spectra of the 1/1 Cu(II) and SGCR solution at pH 7.0 are shown in Fig. 4. The spectra 1, 2 and 3 may be assigned to the complex species $CuSGCR^-$, as discussed above. The spectrum recorded at 298 K shows four lines of the isotropic hyperfine structure from the copper nucleus. However, two lines in the lower field are poorly resolved. At temperatures above 327 K their resolution is much improved and the isotropic hyperfine splitting A_0 was obtained accurately. This means that the molecule of SGCR is large and the molecular tumbling of the complex is slow at room temperature, hence the anisotropic coupling is not averaged out completely.[6]

The spectrum at 77 K shows the well-defined copper hyperfine coupling lines A_z parallel to the external magnetic field direction, defined here as the direction of the Cartesian z-axis. However, the fourth line in the highest field is observed as a shoulder overlapped on the $g_\perp$ structure for the components perpendicular to the external magnetic field. These lines in the highest field are shown in spectrum 3. Several of the lines are not well resolved. These lines may be ascribed to the anisotropic hyperfine splitting, A_x and A_y, as

Table 3. Formation constants of complexes at 25°C and $\mu = 0.1$ (KNO_3)

Ligand	Reaction		log K						
			Mn	Co	Ni	Cu	Zn	Cd	Pb
SGCR	$M^{2+} + L^{3-} \rightleftharpoons ML^-$	K_{ML}	4.6	7.6	8.8	12.8	7.6	6.2	9.1
	$ML^- + L^{3-} \rightleftharpoons ML_2^{4-}$	K_{ML_2}	3.1	5.4	6.1	5.2	5.7	4.3	3.4
	$ML^- + H^+ \rightleftharpoons MHL$	K_{MHL}				5.3			
	$ML^- + OH^- \rightleftharpoons M(OH)L^{2-}$	$K_{M(OH)L}$			3.8*				4.0*

* Measured by spectrophotometry at room temperature; the rest by pH-titration.

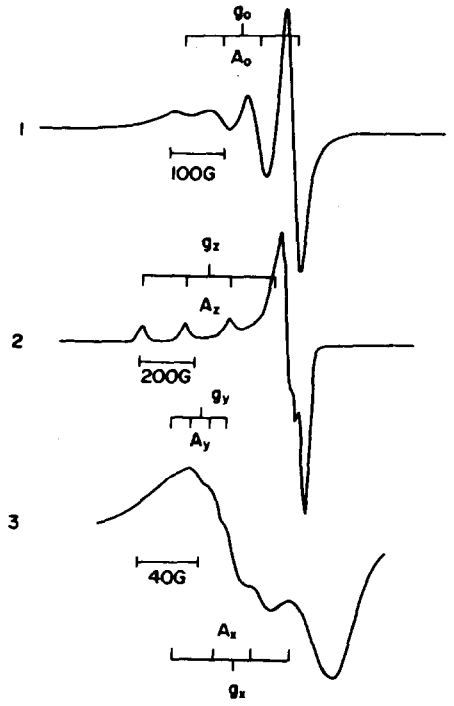


Fig. 4. First-derivative ESR spectra of Cu(II) and SGCR solutions at pH 7.0. Cu(II): 5×10^{-3} *M*, SGCR: 5×10^{-3} *M*. Temperature: *1*–25°C, *2* and *3*–77 K.

indicated in Fig. 4. Each anisotropic *g*-factor, $g_i (i = x, y$ or $z)$ for the three Cartesian axes, was determined from the centre of the corresponding hyperfine splitting and each anisotropic hyperfine constant $A_i (i = x, y, z)$ was determined from averaging the splitting widths of the four lines in spectra 2 and 3. The isotropic *g*-factor and hyperfine constant, g_0 and A_0, were determined similarly from spectrum 1. These values are tabulated in Table 4 together with those for the other complex species. The average values of the anisotropic constants $g_0 = (g_x + g_y + g_z)/3$ and $A_0 = (A_x + A_y + A_z)/3$ obtained from the spectra of $CuSGCR^-$ at 77 K show excellent agreement with the values of the isotropic constants, g_0 and A_0, obtained from the ESR measured at 298 K.

The ESR parameters for the other complex species were determined in the same manner as described above.

The anisotropic *g*-factors, g_x and g_y, and hyperfine constants, $|A_x|$ and $|A_y|$, are almost equal. This indicates that the Cu(II) complexes with SGCR have almost axial symmetry. Therefore, if the Cu(II) complexes have axial symmetry D_{4h}, the following equations would hold:

$$g_z = g_\parallel; \quad A_z = A_\parallel$$
$$g_\perp = (g_x + g_y)/2; \quad A_\perp = (A_x + A_y)/2 \qquad (1)$$

where $g_\parallel$, $A_\parallel$, $g_\perp$ and $A_\perp$ are the components of the anisotropic *g*-factor and hyperfine constant parallel to and perpendicular to the static magnetic field.

If the ligand field transition energies are estimated from the visible-region absorption spectra, the LCAO–MO parameters of the antibonding orbitals in the Cu(II) paramagnetic site can be determined and detailed discussion on the nature of the chemical bond is possible. However, the spectrum arising from the *d*–*d* electron transition of Cu^{2+} is overlapped by the absorption spectrum of SGCR. Therefore, only the LCAO–MO coefficient, α, of the antibonding orbital $\psi_{B_{1g}}$ [equation (2)] was calculated from equation (3).

$$\psi_{B_{1g}} = \alpha d_{x^2-y^2} - \alpha'(-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)})/2 \qquad (2)$$

$$\alpha^2 = \frac{A_\parallel}{P} + (g_\parallel - 2.0023) + \frac{3}{7}(g_\perp - 2.0023) + 0.04 \qquad (3)$$

The symbols in equations (2) and (3) are those described in the literature.[7] B_{1g} represents in-plane σ-bonding and the four donor atoms on the *x* and *y* axes are labelled by superscripts starting with (1) for the *x* axis and proceeding counter-clockwise. The σ-orbitals are hybridized sp^2 orbitals of the donor atoms. For free Cu(II), *P* has the value $-0.036\ cm^{-1}$. $A_\parallel$ usually has a negative sign and its value in gauss is converted into frequency units from the equation

$$A(cm^{-1}) = 4.669 \times 10^{-5}\ gA\ (gauss)$$

The $g_\perp$ and $A_\perp$ values for CuHSGCR and $Cu(SGCR)_2^{4-}$ were calculated from the equations $g_0 = (g_\parallel + 2g_\perp)/3$ and $A_0 = (A_\parallel + 2A_\perp)/3$, and are given in parentheses in Table 4.

Table 4. ESR parameters of Cu(II)–SGCR complexes*

Species	g_0	g_x	g_y	g_z	A_0†	A_x†	A_y†	A_z†	α^2
CuHSGCR	2.141	(2.072)		2.279	66	(21)		156	0.81
$Cu(HSGCR)_2^{2-}$				2.245				154	
$CuSGCR^-$	2.139	2.063	2.079	2.276	67	26	13	162	0.82
$Cu(SGCR)_2^{4-}$	2.128	(2.064)		2.257	59	(19)		140	0.73

* Values omitted were difficult to determine because more than one complex was present and the spectra overlapped. The values in parentheses represented the mean values of the *x*- and *y*-axis components calculated by substituting the other known values into the equation $g_0 = (g_x + g_y + g_z)/3$ or $A_0 = (A_x + A_y + A_z)/3$.

† Measured in gauss.

The value of α^2 is lower for $Cu(SGCR)_2^{4-}$ than $CuSGCR^-$. This trend suggests that a decreasing axial ligand field causes an increase in strength of the in-plane σ-bonding. Hathaway and Billing[8] have discussed the concept of tetragonality, T, which is defined as equal to R_s/R_l, where R_s and R_l are the short and long copper–ligand distances, respectively, and it can be related to the energy of the lowest electronic transition. Pradilla-Sorzanvo and Fackler[9] have discussed in-plane σ-bonding character in terms of tetragonality, T, and indicated that T decreases with decrease in α. This trend, observed for $CuSGCR^-$ and $Cu(SGCR)_2^{4-}$ suggests that the same tetragonal distortion probably occurs in these complexes. The α-value of $Cu(HSGCR)_2^{2-}$ could not be determined because the g_0 and A_0 values were difficult to determine, but g_z and A_z showed the same trend as in $Cu(SGCR)_2^{4-}$ and suggest that the tetragonality T decreases.

Colour change in complex formation

The colour change of an indicator in complex formation is one of the most important factors in its analytical application. The visible-region absorption spectra of the SGCR complexes may be attributed to the electronic π–π^* transition characteristic of the sulphonephthalein group of the SGCR molecule and the change in colour may result from dissociation of protons or the coordination of the phenolic oxygen atom to the metal ion. The greater the colour change on the complex formation, the more useful the practical application. The wavelength shifts for the absorption maximum when the 1:1 complexes $MSGCR^-$ are formed from the species $SGCR^{3-}$ are plotted in Fig. 5 against the quantity E_n^* introduced by Klopman[10] as a measure of the "hardness" of metal ions. The higher E_n^*, the harder the metal ion and the greater its affinity for hard donor atoms.[10,11] The

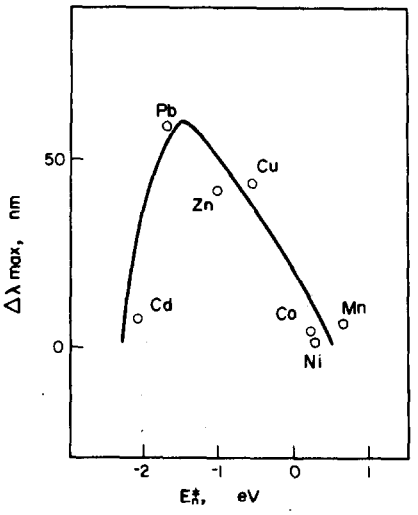
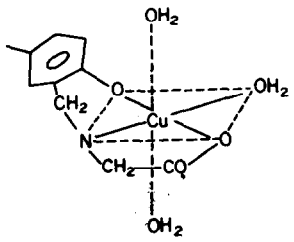


Fig. 5. Plots of $\Delta\lambda_{max}$ for the complex $MSGCR^-$ *vs.* E_n^* for the metal ion. $\Delta\lambda_{max}$ = difference between λ_{max} for the complex $MSGCR^-$ and for $SGCR^{3-}$. E_n^* = hardness of metal ion, 10 eV.

shift in λ_{max} arises from the combination of the localization of π-electron density on the phenolic oxygen atom by the inductive effect of the positively-charged metal ion and/or charge-transfer from the π-electron into the covalent bonding orbital between the phenolic oxygen atom and the metal ion. The extent of the first of these interactions would be increased by increase in the hardness. The value of $\Delta\lambda_{max}$ is maximal at E_n^* *ca.* -1.5 eV because at higher or lower E_n^* values there is a decrease in the ionic and covalent interactions respectively. Thus in terms of colour change, SGCR is most suitable for Pb(II), Zn(II) and Cu(II), which have E_n^* values ranging from -1.5 to -0.5 eV.

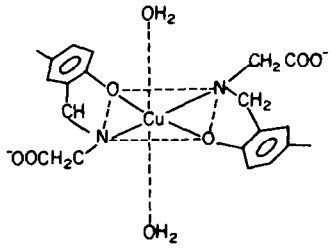
Formation constants and structures of the complexes

The relative values of the formation constants for the 1:1 complexes, $MSGCR^-$, show similar trends to those for a wide variety of ligands having oxygen and/or nitrogen donor atoms, the sequence usually being Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II) and Cd(II) < Pb(II). It is noteworthy that the 1:1 Cu(II) complex with SGCR is especially stable. However, the formation constants for the 1:2 complexes of Cu(II) and Pb(II) do not follow the sequence above. This may be explained in terms of the co-ordination number of the metal ion. The log K_{ML_2}/log K_{ML} ratios are about 0.7, 0.7, 0.7, 0.4, 0.7, 0.7 and 0.4 for Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) respectively. These metals may be divided into two groups according to these ratios. Cu(II) and Pb(II) are in one group and Mn(II), Co(II), Ni(II), Zn(II) and Cd(II) in the other. The co-ordination numbers, CN, of these metal ions in solution are usually 4 or 6. SGCR has three donor atoms, *i.e.*, carboxylic oxygen, phenolic oxygen and imino nitrogen, and therefore, the co-ordination of two SGCR molecules to a metal ion would produce two patterns of behaviour for the formation constants of the 1:2 complexes according to whether the CN was 4 or 6. The ratio log K_{ML_2}/log K_{ML} for a metal ion with CN 4 would be smaller than that for the a metal ion with CN 6 with respect to the terdentate ligand, SGCR, From this point of view, the CN may be 6 for Mn, Co, Ni and Zn and 4 for Pb and Cu. From the discussion above of the tetragonality, T, the in-plane σ-bonding in $Cu(SGCR)_2^{4-}$ is assumed to be increased and the co-ordination distance on the z-axis to be elongated, indicating that the Jahn–Teller stabilization increases.



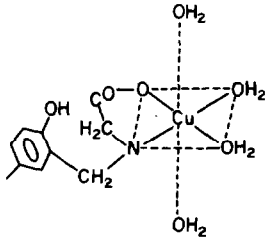
(II) CuSGCR$^-$

However, the stability constant decreases. Therefore, the co-ordination sites on the elongated axis in $Cu(SGCR)_2^{4-}$ are assumed not to be occupied by the donor atoms of SGCR and the structures for $CuSGCR^-$ and $Cu(SGCR)_2^{4-}$ are assumed to be (II) and (III) respectively.

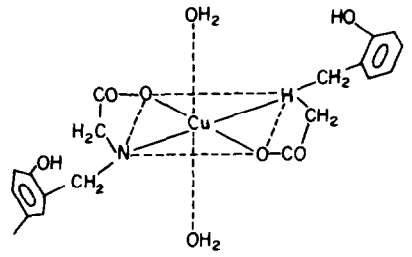


(III) $Cu(SGCR)_2^{4-}$

The relatively small value of log K_{ML_2}/log K_{ML} for Pb(II) is probably due to the tetragonal structure, which is frequently encountered in Pb(II) complexes in aqueous solution. The elongation of one bonding axis in $Cu(HSGCR)_2^{2-}$ is also indicated by the values of the ESR parameter, g_z and A_z. The dissociation of a proton from CuHSGCR to form $CuSGCR^-$ is accompanied by a colour change (λ_{max} changes from 475 to 538 nm). This suggests that the proton of CuHSGCR may be attached to the phenolic oxygen atom and the structure of CuHSGCR may be assumed to be (IV). There are no data for the visible-region absorption spectrum for $Cu(HSGCR)_2^{2-}$, but the proton may again be attached to the phenolic oxygen atom, in acidic media (pH *ca.* 4) and the structure is probably (V).



(IV) CuHSGCR



(V) $Cu(HSGCR)_2^{2-}$

CONCLUSION

Only Cu(II) among the bivalent metal ions investigated here reacts with SGCR in a weakly acidic solution (pH *ca.* 4–6), so SGCR is available as the specific indicator for Cu(II) in such media. In alkaline solution, the colour change is large for formation of the Pb(II), Zn(II) and Cu(II) complexes, and the formation constants are higher than about 10^8; thus SGCR is available as an indicator for these metal ions in alkaline media. However, it is not suitable for use with the other metals investigated here.

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A GENERAL METHOD FOR COULOMETRIC TITRATION OF ALKYLANILINES WITH BROMINE

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Summary—A general method is described for the coulometric titration of alkylanilines with anodically generated bromine. The reaction is carried out in water–acetic acid medium and the reactivity is governed by varying the water content and the concentration of bromide ion and by the addition of pyridine. In this way most types of alkylanilines can be titrated quantitatively. Unlike the case for alkylphenols, the bromine consumption is not always higher in the pyridine-containing media than in the pyridine-free. The bromine consumption is also more dependent on the bromide content of the medium than it is for alkylphenols. The mean relative error, for the best medium for each compound, is ±0.9% for primary alkylanilines, ±0.9% for secondary and ±1.2% for tertiary.

Recently a general method for the coulometric titration of alkylphenols with anodically generated bromine was described in this journal.[1] The present communication deals with a related problem, the coulometric bromination of alkylanilines. Bromination has historically been an important method for the quantitative determination of anilines, especially aniline itself and methylanilines. Non-coulometric bromination methods have utilized direct titration with bromine or bromide–bromate solutions and the endpoint has been detected visually, with or without an internal indicator.[2,3] Starch–iodide paper as an external indicator has also often been employed[4] as have instrumental indication methods, *e.g.*, potentiometric[5] and photometric[6] methods. The most common approach, however, is to use a back-titration where titrant is added in excess and the excess is then determined iodometrically.[7] The reason for the frequent application of the back-titration method is the sluggish reaction of many anilines with bromine under the conditions generally used.

The variety of methods employed demonstrates the difficulty of developing a general bromination method for alkylanilines. An example of this is given by Day and Taggart[8] who tried in vain to develop universally applicable bromination methods for phenols and aromatic amines. Of a number of alkylanilines investigated, only aniline and *m*-toluidine could be determined with sufficient accuracy, although direct as well as indirect methods were utilized. In a more recent investigation Matrka *et al.*[9] studied the quantitative bromination of several *N*-alkylanilines in 1*M* hydrochloric acid. The direct bromination method was too slow to be useful and only *N*-methylaniline could be determined by the back-titration method. Oxidative side-reactions also took place whereby alkyl groups were split off. The reason for the problems encountered is thought to lie mainly in the choice of titration medium. Although aqueous media are most common, brominations of alkylanilines have also been performed in glacial acetic acid[10] and in propylene carbonate.[11]

Examples of coulometric bromination methods applied to alkylanilines are scarce. Buck and Swift[12] seem to have been the first to utilize a coulometric bromometric titration method for the determination of aniline. Bromine was generated in excess, and back-titrated with electrolytically generated copper(I). The titration medium was an acidified aqueous solution. The back-titration mode was necessitated by the slow reaction between aniline and bromine under the conditions used. In a more extensive coulometric investigation Delgado[13] titrated aniline and *o*- and *p*-toluidine. The reaction was governed by regulation of the pH. Thus, while aniline could be quantitatively brominated in the pH range 1–5, the toluidines had to be titrated at pH 1. *N*,*N*-Dimethylaniline could not be titrated because the reaction was too slow. The titration was followed biamperometrically with two platinum electrodes and the indicator currents were plotted manually against time.

The aim of the present investigation was to develop a general coulometric method usable for the quantitative determination of all kinds of alkylanilines. In our previous communication[1] an extensive study was made of various factors influencing the quantitative bromination reaction of phenols, *i.e.*, composition of titration medium, amount of substance titrated and magnitude of generating current and polarizing resistance. It was found that the conclusions drawn from this investigation were also valid for the quantitative coulometric bromination of alkylanilines. Accordingly, aqueous acetic acid was used as titration medium. The reactivity-promoting properties of the media were regulated by varying the proportions of acetic acid and water and the bromide concentration. To some media pyridine was added in order to accelerate the bromination reaction (see Table 1).

Table 1. Composition of media used for bromination of anilines

Medium	Acetic acid, % v/v	Water, % v/v	Pyridine, % v/v	[Br^-], M
I-1	55	35	10	0.1
I-2	55	35	10	0.4
I-3	55	35	10	1.2
II-3	55	40	5	1.2
III-1	60	40	—	0.1

EXPERIMENTAL

Apparatus

The apparatus has already been described[1] and was used without change. The generating current was 3 mA, the polarizing resistance 100 kΩ and the chart-speed 30 mm/min.

Reagents

Anilines. These were of the best grade commercially available. Some of them were further purified by distillation or recrystallization. *N,N*-2,6-Tetramethylaniline and *N,N*-2-triethylaniline were prepared in the laboratory.[14]

Acetic acid. Merck, 99–100%.

Sodium bromide. Sodium bromide, 99%, BDH.

Pyridine. Mallinckrodt analytical grade.

Titration procedure

The details have already been published,[1] the only change being use of methanol instead of acetic acid for dissolving the sample. The reason for this is the risk of partial acetylation of primary and secondary anilines with the formation of unreactive *N*-acetylanilines. An amount of amine was taken each time which would consume between 10 and 20 μeq of bromine (*i.e.*, required 5–10 min generation at 3 mA).

RESULTS AND DISCUSSION

Thirty-nine anilines were titrated by the coulometric bromination method. Of these 17 were primary anilines (Table 2), 12 secondary anilines (Table 3) and 10 tertiary anilines (Table 4). The results of the brominations have been summarized in Table 5 and are the means of at least two titrations.

Primary anilines

All the primary anilines investigated could be titrated in the pyridine-free medium III-1, containing 60% v/v acetic acid and 0.1*M* with respect to bromide (see Table 1). The reaction between aniline and bromine is somewhat sluggish in this medium, giving low results. On that account the pyridine-containing media I-1 or II-3 are recommended. As seen from Table 2, all free *ortho* and *para* positions are substituted by bromine whether the medium contains pyridine or not. It is noteworthy that pyridine is not necessary for full bromination. In the previous investigation of phenols it was generally found that monobromination took place in pyridine-free media, while a pyridine-containing medium was required for full bromination.

In this case it was even found that less bromine was consumed by aniline in the pyridine-containing medium II-3 (2 moles of Br/mole) than in the pyridine-free medium III-1 (3 moles of Br/mole) and the titration could be carried out with a precision better

Table 2. Results of bromination of primary alkylanilines

Aniline	Titn. medium	Number of H substituted	Mean error, %	Titn. medium	Number of H substituted	Mean error, %
$C_6H_5NH_2$	III-1	3	−4.5	I-1	3	−1.6
	—	—	—	II-3	2	−0.8
$C_6H_5NH_2$, HCl	III-1	3	−4.0	I-1	3	−2.5
2-Me	III-1	2	+0.4			
2-Et	III-1	2	−1.0			
2-isoPr	III-1	2	−0.8			
3-Me	III-1	3	+0.1	I-1	3	−0.5
3-Et	III-1	3	−0.1			
3-Et, HCl	III-1	3	−0.9			
4-Me	III-1	2	−0.3	I-1	2	+0.4
4-Et	III-1	2	+0.8			
4-Et, HCl	III-1	2	−0.9			
4-isoPr	III-1	2	−0.8			
4-Bu	III-1	2	−0.2	I-1	2	−0.2
2,3-diMe	III-1	2	−0.4			
2,4-diMe	III-1	1	+1.1			
2-Me-4-Bu	III-1	1	−2.5	I-3	1	−1.6
2,5-diMe	III-1	2	−0.7			
2,6-diMe	III-1	1	+0.8			
3,4-diMe	III-1	2	+0.5			
2,4,6-triMe	III-1	0	—	I-1	1	+3.4

Table 3. Results of bromination of secondary alkylanilines

Aniline	Titn. medium	Number of H substituted	Mean error, %	Titn. medium	Number of H substituted	Mean error, %
N-Me	III-1	2	−0.6	I-2	2	−0.6
N-Et	III-1	2	−1.4	I-2	2	−0.8
N-Pr	III-1	2	−1.3	I-3	2	−0.8
N-Bu	III-1	2	−1.3	I-2	2	−1.0
N-Bz	III-1	2	−2.8	I-1	2	−1.9
N-Ph	III-1	4	−3.7	I-1	4	−3.0
N-Me-2-Me	III-1	2	*	I-1	2	−0.6
N-Et-2-Me	III-1	1	+2.1	I-1	2	+0.1
N-Me-4-Me	III-1	2	*	I-1	2	+1.0
N-Et-4-Me	III-1	0	—	I-1	2	−0.2
N-Et-3-Me	III-1	2	−0.6	I-1	3	−1.4
N-Me-3-Me	III-1	2	+0.8	I-1	3	−2.8
				I-3	2	−1.3

* Sloping titration curve, difficult to evaluate.

than 1%. We believe this fact to be due to the higher bromide content in the former case (1.2*M* against 0.1*M*) which for anilines has a greater influence on the reactivity than the presence or absence of pyridine.

2,4,6-Trimethylaniline does not react with bromine in the pyridine-free medium III-1, but in the pyridine-containing medium I-1 it consumes one mole of bromine per mole of aniline. The reaction of this compound with bromine, in spite of the fact that it has no free *ortho* and *para* positions, should be compared with the corresponding reaction between 2,4,6-trimethylphenol and bromine. In the latter case a *para*-quinoid bromocyclohexadienone is formed and it is believed that an analogous compound results from the reaction between 2,4,6-trimethylaniline and bromine. Although in most cases results of similar accuracy were obtained in media with and without pyridine, it was often observed that the titration curve in the pyridine-containing media was steeper after the end-point, which facilitated the detection of the end-point (*cf.* Fig. 1 in ref. 1).

The reaction between some primary anilines and bromine in medium IV,[1] containing 10% v/v water but no pyridine, was also studied. It appeared that in this medium aniline, 2-methylaniline and 3-methylaniline were monobrominated while 4-methylaniline did not react, indicating that the bromine entered the *para* position. However, the results are not communicated in Table 2 as they were only approximate. This difference in reactivity could be used to distinguish between 2- and 3-alkylanilines on the one hand and 4-alkylanilines on the other.

Table 2 also includes some titration results for hydrochlorides of primary anilines. As might be expected, they can be titrated just as well as the free amines in acetic acid–water media. This is of interest as anilines are often isolated and purified as their hydrochlorides.

Secondary anilines

Secondary anilines, like the primary, can be titrated in medium III-1 (with some exceptions) or in one of the media of group I (see Table 3). However, the behaviour of secondary anilines is different from that of the primary ones. Thus, in secondary anilines without nuclear substituents bromine generally enters only two of the three vacant *ortho* and *para* positions, irrespective of whether the medium contains pyridine (I) or not (III-1). For secondary anilines with nuclear alkyl groups in the *ortho* or *para* positions a further decreased reactivity is observed in medium III-1. This is sometimes shown by a sloping titration curve, which makes it difficult to evaluate the end-point accurately or, as for *N*-ethyl-4-methylaniline, by absence of reaction. Secondary anilines with a methyl group in the *meta* position are as reactive in medium III-1 as secondary anilines without nuclear alkyl groups, bromine entering two of the three vacant *ortho* and *para* positions.

In the pyridine-containing medium I-1 the reactivity of the nuclear-substituted secondary anilines is greater than in medium III-1. Thus all compounds gave some reaction, and all hydrogen atoms in free *ortho* and *para* positions were exchanged for bromine as compared to one hydrogen atom less in medium III-1 for the anilines which did react in this medium. Another example of the influence of the bromide concentration in the medium is given by the reaction of *N*-methyl-3-methylaniline for which the number of entering bromine atoms is lowered from three to two when the bromide concentration is increased from 0.1*M* (I-1) to 1.2*M* (I-3).

Tertiary anilines

The decreased reactivity towards bromine previously observed for secondary anilines is further accentuated for tertiary anilines (see Table 4). Thus

Table 4. Results of bromination of tertiary alkylanilines

Aniline	Titn. medium	Number of H substituted	Mean error, %	Titn. medium	Number of H substituted	Mean error, %
N,N-diMe	III-1	1	+1.0	I-1	2	±0.0
N,N-diEt	III-1	1	−1.3	I-3	1	+2.3
N,N-diPh	III-1	3	−0.6	I-1	3	−0.2
N,N-diMe-2-Me	III-1	0	—	I-2	1	+2.8
N,N-diEt-2-Me	III-1	0	—	I-1	0	—
N,N-diEt-2-Et	III-1	0	—	I-1	0	—
N,N-diMe-3-Me	III-1	1	−0.7	I-1	2	−0.6
N,N-diEt-3-Me	III-1	1	−1.2	I-1	2	−3.7
N,N-diMe-4-Me	III-1	0	—	I-1	1	+3.6
N,N-diEt-4-Me	III-1	0	—	I-1	1	+0.1

in the pyridine-free medium III-1 only compounds without nuclear substituents or with a methyl group in the *meta* position react. Only one bromine atom enters each benzene ring, probably in the *para* position.

In the pyridine-containing media I, all the compounds tested except two, namely *N,N*-diethyl-2-methylaniline and *N,N*-diethyl-2-ethyl-aniline gave some reaction. The number of hydrogen atoms substituted varies with the structure. In tertiary anilines without nuclear substituents, bromine enters one or two of the three vacant *ortho* or *para* positions, depending on the size of the groups at the nitrogen atom. Thus, in *N,N*-dimethylaniline two hydrogen atoms are exchanged and the titration can be performed in medium I-1. Attempts to titrate *N,N*-diethylaniline in the same medium showed that approximately two moles of bromine were consumed per mole of determinant, but the values were too low to be useful for quantitative determination. However, a change to medium I-3 where one mole of bromine was consumed per mole, gave a quantitative result. We have here another example of the marked influence of the bromide concentration in the medium on the bromine consumption. As can be seen from Table 4, the pyridine-free medium III-1, in which the reacting ratio is likewise 1:1, is the best choice for the determination of this compound. The third tertiary aniline without nuclear substituents in Table 4, triphenylamine, consumes one molecule of bromine per benzene ring in the most bromination-promoting medium I-1 just as in medium III-1.

Of the nuclear-substituted tertiary anilines, those with substituents at the *ortho* and *para* positions consume one mole of bromine per mole or do not react at all in media of group I. The unreactive compounds, *N,N*-diethyl-2-methylaniline and *N,N*-diethyl-2-ethylaniline are the only anilines in this investigation which did not react in any of the media investigated. Obviously anilines in which the steric interaction between the substituents at the nitrogen atom and an *ortho*-situated group is great enough must be expected to be unreactive towards bromine. The two nuclear-substituted compounds with methyl groups in the *meta* position consume two moles of bromine per mole in medium I-1 against one in medium III-1.

In addition to the tertiary anilines listed in Table 4, *N,N*-dimethyl-2,6-dimethylaniline was also titrated with bromine. This compound did not react in the pyridine-free medium III-1, but consumed between three and four moles of bromine per mole in the pyridine-containing medium I-1. However, the latter reaction, which we believe to be due to oxidation, is not useful for quantitative determination.

The secondary and tertiary anilines are less reactive than the primary anilines because of the steric interaction between substituents on the nitrogen atom and *ortho*-situated groups existent in these compounds or in their bromination products. The nuclear substituent can be an alkyl group or a bromine atom. It is known that this steric hindrance interferes with the alignment between the nitrogen atom and the plane of the benzene ring, thereby decreasing the activation which arises from resonance of the *ortho* and *para* positions.[15]

In Table 5 the results of the bromination of aniline and alkylanilines have been summarized. The decreased reactivity towards bromine in the series primary–secondary–tertiary anilines is clearly demonstrated. It is also seen that pyridine exerts a bromination-promoting effect only for secondary anilines with nuclear substituents and for tertiary anilines. Likewise it is evident that among nuclear-substituted secondary and tertiary anilines the *meta*-substituted are generally most reactive.

Differentiation between anilines by acetylation and bromine titration

When a primary or secondary aniline is acetylated, it loses its ability to react with bromine in the coulometric titration method. This fact can be utilized for distinguishing these types of anilines from tertiary ones. Thus an aniline which can react with bromine before acetylation but not after heating for a couple of minutes with an excess of acetic anhydride, is either primary or secondary. Because of the possibility of acetylation the use of aqueous acetic acid as titration medium can be questioned. However, we have not

Table 5. Media for quantitative bromination of alkylanilines

Type of aniline	Medium	Number of available hydrogen atoms exchanged for bromine
Primary		
With and without substituents	III-1 or I	All
	II-3*	2 of 3
Secondary		
Without nuclear substituents	III-1 or I	2 of 3
With nuclear substituents		
in 3-position	III-1	2 of 3
	I-1	All (3)
in 2- or 4-position	III-1	Not recommended†
	I-1	All (2)
Tertiary		
Without nuclear substituents	III-1	1 of 3
	I	2 or 1 of 3
With nuclear substituents		
in 3-position	III-1	1 of 3
	I-1	2 of 3
in 2- or 4-position	III-1	None
	I	1 of 2, or none

* Aniline.
† See Table 3.

noted any adverse effects of this titration medium on the bromination reaction of primary and secondary anilines and consequently conclude that no acetylation takes place under the conditions used (see also "Experimental").

CONCLUSIONS

It is concluded that nearly all kinds of alkylanilines can be titrated quantitatively with coulometrically generated bromine in water–acetic acid media, with or without added pyridine. The standard titration media are the pyridine-free medium III-1 and the pyridine-containing media of group I. The former is well suited for the determination of primary anilines except aniline while secondary and tertiary anilines are better determined in the pyridine-containing media. Not all of the anilines investigated can be determined. Tertiary anilines with alkyl groups in one or both of the *ortho* positions may give no reaction, or may react to give irreproducible results, as exemplified by some compounds in Table 4.

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COULOMETRIC TITRATION OF ANILINES, MAINLY CONTAINING DEACTIVATING FUNCTIONAL GROUPS, WITH BROMINE

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Summary—A general method is described for the coulometric titration of various substituted anilines with anodically generated bromine. The reaction is carried out in water–acetic acid medium and the reactivity is governed by varying the water content and the bromide concentration, and by the addition of pyridine. In this way the majority of the substituted anilines tested can be titrated quantitatively. There is no great difference in the reactivity-promoting properties of pyridine-free and pyridine-containing media, but the latter generally give the better results and are therefore to be preferred. The mean relative error, for the best medium for each compound, is ±0.5% for the haloanilines and ±1.0% for anilines with oxygenated functional groups.

In a previous paper[1] a general method was described for the coulometric titration of alkylanilines with anodically generated bromine. This paper deals with the coulometric bromination of anilines, mainly those containing deactivating groups. Non-coulometric bromination methods have previously been applied to several deactivated anilines with varying success, while coulometric bromination methods have been used only very occasionally. Kalinowski and Zwierzchowski[2,3] seem to have been the first to utilize coulometric bromometric titration for the determination of deactivated anilines. They titrated *p*-aminobenzoic acid and novocaine, an ester of *p*-aminobenzoic acid, in aqueous sulphuric acid. The titration was followed biamperometrically with two platinum electrodes and either a known excess of bromine was generated, or the substance was titrated directly to the end-point. Delgado[4] titrated *o*- and *p*-aminobenzoic acid and sulphanilic acid, likewise in aqueous solution, and the reaction was governed by regulation of the pH. The titration was followed biamperometrically with two platinum electrodes and the indicator currents were plotted manually against time.

In this investigation a thorough study has been made of the application of the coulometric bromometric titration method, originally developed for phenols,[5,6] to the determination of anilines containing various functional groups, mainly deactivating. The following groups are included: halogen, methoxy, formyl, acetyl, carboxyl, ester, carboxymethyl (CH_2COOH), nitro and sulphonate. Aqueous acetic acid was used as titration medium for the majority of the compounds investigated and the reactivity-promoting properties of the media were regulated by varying the content of acetic acid and water and the concentration of bromide ion. To some media pyridine was added in order to promote the bromination reaction (see Table 1).

EXPERIMENTAL

Apparatus

The apparatus has been described previously[5] and was used without change. The generating current was 3 mA, the polarizing resistance 100 kΩ and the chart-speed 30 mm/min.

Reagents

The anilines used were of the best grade commercially available. Some of them were further purified by distillation or recrystallization. The other reagents were as described before.[1]

Titration procedure

For details of the titration procedure, see the earlier work,[5] the only change being use of methanol instead of acetic acid for dissolving the sample, because of the risk of acetylation of primary and secondary anilines with the formation of non-reactive acetanilides.[1] In the case of aminosulphonic acids water is used as the solvent.

An amount of amine is weighed out which is calculated to consume about 20 μeq of bromine for full bromination. Generally the break in the titration curve corresponding to full bromination is taken as the end-point. In most instances the results are not much dependent on the amount of substance titrated, provided that the bromine consumption lies in the range 10–20 μeq.

In cases where the titration curve has two breaks it is sometimes necessary to use the first for evaluation of the end-point. The break used is given in the appropriate column in the tables, in parentheses. The number of hydrogen atoms substituted given in the tables always corresponds to the break utilized for end-point evaluation, irrespective of whether the first or second break is used.

There are two main reasons for failure of the bromometric titration method, and these are evident from the appearance of the titration curve. Thus, the break in the titration curve, although reproducible and corresponding to the consumption of a whole-number reaction ratio, may be too small for accurate evaluation of the end-point. Another cause of failure is that the break, although steep enough, is not reproducible or gives erroneous results. The results given in the tables are the average of at least two titrations. As seen from the column giving the number of hydrogen atoms substituted, some amines are only partly

Table 1. Composition of media used for bromination of anilines

Medium	Acetic acid, % v/v	Water, % v/v	Pyridine, % v/v	$[Br^-]$, M
I-1	55	35	10	0.1
I-2	55	35	10	0.4
I-3	55	35	10	1.2
III-1	60	40	—	0.1

substituted by bromine at the free *ortho* and *para* positions by the time the end-point is reached, but more bromine is often consumed after this, since the titration curve does not immediately return to the baseline after the end-point (see Tables 2 and 3).

RESULTS AND DISCUSSION

About fifty substituted anilines were titrated in medium III-1 and also in one or several of the media of group I (see Table 1). Nearly all the anilines were primary, and only two tertiary anilines were included. In a previous study on the coulometric bromometric titration of phenols containing deactivating functional groups[6] it was found that these compounds required pyridine-containing media, *i.e.* from groups I or II, for quantitative bromination. For the corresponding anilines this is not the case. They can be titrated in pyridine-free as well as pyridine-containing media, but the best results were generally obtained in the latter, which accordingly are to be preferred.

Another difference between the behaviour of phenols and anilines containing deactivating groups was that while the strongly deactivated phenols such as trichloro- and dinitrophenols could be quantitatively brominated, this was not the case for the corresponding anilines. The latter compounds either did not consume bromine at all or gave sloping titration curves from which the end-point could not be properly evaluated. The marked dependence of the reactivity of anilines on the bromide concentration in the medium, which was previously observed for alkylanilines,[1] was found also to exist for the types of anilines studied in this work.

Haloanilines

Most haloanilines can be titrated with fair accuracy in the pyridine-containing media I-1 and/or I-3 (see Table 2). For comparison, a titration was also performed in the pyridine-free medium III-1. Although results of comparable accuracy are reported in several cases for media of groups I and III in Table 2, medium III-1 tended to give sloping titration curves which were difficult to evaluate accurately.

As can be seen from Table 2, *ortho*- and *para*-sub-

Table 2*. Results of bromination of haloanilines

Aniline	Titn. medium	Number of H substituted	Number of breaks in the titration curve	Mean relative error, %	Titn. medium	Number of H substituted	Number of breaks in the titration curve	Mean relative error, %
2-Fluoro	I-1	2	1	−0.8	III-1	2	1	−2.6
3-Fluoro	I-3	2	1	−0.5	III-1	2	1	+2.3
4-Fluoro	I-1	2	1	−0.2	III-1	1-2	1	†
2,4-Difluoro	I-1	1	1	−0.6	III-1	~1	1	†
2,5-Difluoro	I-3	1	1	+0.4	III-1	1	1§	+1.7
2-Chloro	I-1	2	2(2)	+0.3	III-1	2	2(2)	−1.5
2-Chloro-6-methyl	I-1	1	1	+0.2	III-1	1	1	+0.3
3-Chloro	I-3	2	1	−0.3	III-1	2	2(1)§	+0.3
3-Chloro-2-methyl	I-1	2	1	−0.6	III-1	2	1	−0.5
3-Chloro-4-methyl	I-1	2	1	−0.7	III-1	2	1	−1.3
5-Chloro-2-methyl	I-1	2	1	+0.4	III-1	2	1	−0.3
4-Chloro	I-1	2	2(2)	−0.8	III-1	~2	1	†
2,3-Dichloro	I-3	1	1§	+0.4	III-1	~1	2(1)§	†
2,4-Dichloro	I-1	1	1	+0.1	III-1	~1	1	†
2,5-Dichloro	I-3	1	1	−0.7	III-1	1	2(1)§	+0.4
2,6-Dichloro	I-1	1	1	+1.0	III-1	1	1	−0.7
3,4-Dichloro	I-3	1	1	+1.0	III-1	~1	2(1)§	†
3,5-Dichloro	I-1	2	1§	+0.6	III-1	2	1	+0.1
2,3,4-Trichloro	I-1	~1	1	†	III-1	~1	1	†
2,4,5-Trichloro	I-1	~1	1	†	III-1	~1	1	†
2-Bromo	I-1	2	2(2)	−2.6	III-1	~2	2(2)	†
	I-3	1	1§	+0.2				
3-Bromo	I-3	2	1	+0.3	III-1	~2	2(1)§	†
4-Bromo	I-1	2	2(2)	−2.5	III-1	~2	1	†
	I-3	1	1§	−0.3				
2,4-Dibromo	I-1	1	1	+1.4	III-1	1	1	−0.3
2-Iodo	I-1	2	2(2)	+0.9	III-1	2	2(2)	+0.2
4-Iodo	I-1	~2	2(2)	†	III-1	~2	2(2)	†

* See also "Experimental".
† Mean relative error greater than 3%.
§ Further bromine consumption after the break used for determination of end-point.

stituted fluoro- and chloroanilines without nuclear alkyl groups are best titrated in medium I-1 if they possess no *meta*-situated halogen atom, and in medium I-3 if they do have one. In the former case bromine enters all vacant *ortho* and *para* positions, in the latter case the number of hydrogen atoms exchanged is one less than the number of available *ortho* and *para* positions. However, for 2,3-dichloroaniline a further consumption of bromine after the end-point can be seen. If the haloaniline contains, in addition to a chlorine atom in the *meta*-position, a methyl group in the *ortho* or *para* position, the titration should be done in medium I-1. The same is valid for 3,5-dichloroaniline. While the methylanilines are fully substituted, only two of the three available positions in 3,5-dichloroaniline are taken up by bromine.

The considerable difference in reactivity-promoting properties between the I-1 and I-3 media for haloanilines is exemplified by the reactions of some chloroanilines with bromine in the two media. Thus, in 4-chloro-, 2,5-dichloro- and 2,4-dichloroaniline one hydrogen atom less is exchanged for bromine in medium I-3 than in medium I-1. This means that the last-mentioned compound does not react in medium I-3. For the two other compounds, only the best values are given in Table 2. As the two media differ only in the bromide concentration, we have here another example of the marked influence of this factor on the reactivity for anilines, previously established for alkylanilines.[1] Other examples follow.

It has not been possible to brominate quantitatively the two trichloroanilines, 2,3,4- and 2,4,5-trichloroaniline, in any of the media used in this work. They do not react at all in medium I-3, and while approximately one mole of bromine is consumed per mole in medium I-1, the results are 5–10% low, and still lower values were obtained in medium III-1.

Bromoanilines react like their fluoro and chloro analogues. However, for 2- and 4-bromoaniline the reaction is somewhat sluggish in medium I-1, giving low results. The titration is better performed in medium I-3, where a useful break is obtained when one hydrogen atom is substituted.

Only two iodoanilines were titrated, namely 2- and 4-iodoaniline. Of these only the first could be brominated quantitatively, two bromine atoms entering the molecule when media I-1 and III-1 were used. It thus behaved like the other 2-halo-substituted anilines. 4-Iodoaniline reacted sluggishly and gave a sloping titration curve from which the end-point could not be accurately evaluated. The reason for this is not known, but it was observed that the electrodes were easily contaminated in this case. A similar behaviour was found for 2- and 4-iodophenol in a pre-

Table 3*. Results of bromination of anilines containing various oxygenated functional groups

Aniline	Titn. medium	Number of H substituted	Number of breaks in the titration curve	Mean relative error, %	Titn. medium	Number of H substituted	Number of breaks in the titration curve	Mean relative error, %
2-Methoxy	I-2	2	1	±0.0	III-1	2	1	+1.0
4-Methoxy	I-media	†	†	†	III-1	2	1	+0.8
2-Formyl	I-3	~1	1‡	§	III-1	1	2(1)‡	+1.5
3-Formyl	I-2	2	2(2)	−0.5	III-1	~2	1	§
N,*N*-Dimethyl-4-formyl	I-1	1	1	+1.7	III-1	~1	1	§
4-Acetyl	I-3	1	1	+1.5	III-1	~2	2(2)	§
4,4'-Bisdimethyl-aminobenzo-phenone	I-1	2	1	+1.3	III-1	1–2	1	§
2-Carboxy	I-3	2	2(2)	+0.9	III-1	2	1	−0.1
3-Carboxy	I-1	3	1	−1.0	III-1	~2	1	§
N,*N*-Dimethyl-3-carboxy	I-1	~1	1	§	III-1	1	1	±1.4
4-Carboxy	I-1	2–3	2(2)	§	III-1	2	2(2)	±0.6
2-Carbomethoxy	I-3	1	1‡	+1.5	III-1	~2	2(2)	§
4-Carboethoxy	I-3	1	1‡	+0.8	III-1	1–2	2(2)	§
4-Carboxy-methyl	I-1	2	1	−1.7	III-1	~2	1	§
2-Sulphonic acid	I-1	2	1	−0.5	III-1	2	1	−0.5
3-Sulphonic acid	I-1	2	1	−1.7	III-1	~2	1	§
4-Sulphonic acid	I-1	2	2(2)	−0.3	III-1	2	1	−0.1
2-Nitro	I-1	1	1	−0.9	III-1	~1	1	§
3-Nitro	I-2	~1	1‡	§	III-1	~1	1	§
4-Nitro	I-1	1	1	−0.4	III-1	1	1	−0.4
Dinitro-(2,4-,2,6-,3,5-)	I-media	0	0	—	III-1	0	0	—

* See also "Experimental".
† Not possible to determine from the titration curve.
§ Mean relative error greater than 3%.
‡ Further bromine consumption after the break used for determination of end-point.

vious investigation, neither compound being brominated quantitatively.[6] The mean relative error for the haloanilines titrated, for the best medium for each compound, is ±0.5%.

Anilines with various oxygenated functional groups

The anilines covered in this section contain methoxy, formyl, acetyl, carboxyl, ester, carboxymethyl (CH_2COOH), sulphonic acid and nitro groups in addition to the amino group. They are on the whole more difficult to determine than the haloanilines, which is also reflected in the results, which are less accurate than those obtained for the haloanilines (see Table 3). The reasons for this are *inter alia* that several of the anilines are sensitive to oxidation and are accordingly easily transformed during storage. Bromine can also oxidize the compounds, or displace some substituent groups such as formyl, carboxyl and sulphonic acid groups, causing overconsumption of titrant.[4]

Methoxyanilines. These anilines differ from the other compounds in Table 3 in having an activating functional group in addition to the amino group. Of the two compounds investigated, 2-methoxyaniline could be titrated without difficulty in pyridine-containing as well as in pyridine-free media, whereas 4-methoxyaniline produced a sloping titration curve in the former type of medium, from which the end-point could not be evaluated. The fact that the solution turned lilac indicated that some secondary reaction was taking place, probably oxidation. Bromine entered all free *ortho* and *para* positions.

Anilines with formyl and keto groups. With one exception these compounds are best titrated in pyridine-containing media of group I. The exception was 2-aminobenzaldehyde which gave a low value in these media. In medium III-1 two breaks were obtained in the titration curve. The first break corresponded to the substitution of one hydrogen atom by bromine and, although small, was usable for evaluation of the end point. The second break corresponded to the substitution of about 1.7 hydrogen atoms and was not useful for quantitative analysis.

With the exception of this compound, the number of hydrogen atoms exchanged in each aromatic ring was one less than the number of available *ortho* and *para* positions.

Anilines with carboxyl and ester groups. For the quantitative bromination of these groups of substituted anilines, pyridine-containing as well as pyridine-free media are necessary. Thus, 4-carboxyaniline and *N,N*-dimethyl-3-carboxyaniline could only be titrated in the pyridine-free medium III-1. For these compounds there is a considerable overconsumption of bromine in pyridine-containing media, which for 4-carboxyaniline is due to partial displacement of the carboxyl group by bromine. Delgado[4] has demonstrated that the decarboxylation of *p*-aminobenzoic acid on bromination in aqueous media is a function of pH. Decarboxylation increases when the pH is raised and becomes quantitative at pH 5. Obviously, the presence of pyridine in medium I-1 raises the pH enough to cause a partial displacement of the carboxyl group by bromine during the titration, as the values are 15–20% too high. In the absence of pyridine, in medium III-1, no displacement of the carboxyl group occurs.

Delgado reported a similar decarboxylation for *o*-aminobenzoic acid in aqueous media at pH 3–5, while in this work only a slight overconsumption of bromine was observed for this compound in the pyridine-containing medium I-3. It is of interest to compare the results obtained for 3-carboxyaniline and its *N,N*-dimethyl derivative. The presence of the two methyl groups at the nitrogen atom decreases the number of bromine atoms entering the ring, from three to one in medium I-1 and from two to one in medium III-1. Similar results were previously observed for the corresponding 3-methylanilines where the decrease in medium I-1 was from three to two and in medium III-1 from three to one.[1]

The two anilines substituted by ester groups, 2-carbomethoxy- and 4-carboethoxyaniline, should be titrated in medium I-3 where the end-point corresponds to entry of one bromine atom into the molecule. However, a further consumption of bromine is evident from the appearance of the titration curve.

Anilines with sulphonic acid and nitro groups. Anilines with sulphonic acid groups in the *ortho* or *para* position can be titrated in pyridine-containing (I-1) as well as pyridine-free (III-1) media with good accuracy while, for metanilic acid, pyridine must be present in the medium if quantitative results are to be obtained. In view of the deactivation exerted by the sulphonic acid group it is somewhat surprising to find that in the 2- and 4-amino sulphonic acids all free *ortho* and *para* positions are substituted by bromine in both pyridine-containing and pyridine-free media. In the corresponding *meta* isomer two of the three vacant positions are substituted.

Nitroanilines are strongly deactivated and not very prone to react with bromine. Thus, of the six compounds tested only 2- and 4-nitroaniline gave quantitative results, the three dinitroanilines did not react, and 3-nitroaniline failed to react quantitatively. For the mononitroanilines only one bromine atom entered the aromatic ring.

In order to facilitate the correct choice of titration medium for the quantitative bromometric titration of substituted anilines, Table 4 has been included. In cases where two media give results of comparable accuracy, the second best medium has been put in parentheses.

Comparison of reactivity of various kinds of anilines with bromine

It is of interest to compare the reactivity towards bromine, in the same medium, of various types of anilines studied in this and in a previous investigation.[1] Table 5 gives the substituent group and the

Table 4*. Media for quantitative bromination of substituted anilines.

Functional group	Medium	Functional group	Medium
Halogen (2- or 4-)		Methoxy (2-)	I-2
F	I-1	Methoxy (4-)	III-1
Cl	I-1	Formyl (2-)	III-1
Br	I-3	Formyl (3-)	I-2
I (2-)	III-1	Acetyl (4-)	I-3
Halogen (3-)		Carboxyl (2-)	II-1
F	I-3	Carboxyl (3-)	I-1
Cl	I-3 (III-1)	Carboxyl (4-)	III-1
Br	I-3	Ester (2-)	I-3
Halogen (di)		Ester (4-)	I-3
Cl (2,3-)	I-3	Carboxymethyl (4-)	I-1
F (2,4-)	I-1	Sulphonic (2-)	I-1 (III-1)
Cl (2,4-)	I-1	Sulphonic (3-)	I-1
Br (2,4-)	III-1	Sulphonic (4-)	III-1 (I-1)
F (2,5-)	I-3	Nitro (2-)	I-1
Cl (2,5-)	III-1 (I-3)	Nitro (4-)	I-1 (III-1)
Cl (2,6-)	III-1 (I-1)		
Cl (3,4-)	I-3		
Cl (3,5-)	III-1 (I-1)		

* See also text.

number of bromine atoms entering the molecule, when the bromination is performed in the pyridine-free medium III-1 containing 60% v/v of acetic acid. Certain conclusions can be drawn from this table.

When the substituent is in the 2- or 4-position relative to the amino group in a primary aniline there is no great difference in reactivity between compounds with activating (Me or MeO) and deactivating groups, hydrogen at the free *ortho* and *para* positions being exchanged for bromine, with some exceptions. Thus for anilines with certain deactivating groups, *i.e.*, formyl and nitro groups, the number of hydrogen atoms exchanged falls to one. Another factor which can decrease the number of entering bromine atoms is the presence of alkyl groups at the nitrogen atom (secondary and tertiary anilines). The size and number of alkyl groups at the nitrogen atom control the number of entering bromine atoms.

When the substituent group is situated in the 3-position there is a difference between anilines with activating (Me) and deactivating groups. In the former case bromine enters all free *ortho* and *para* positions (3), in the latter, one less (2). The reason for this should be sought in the fact that a *meta* methyl group is in a position to activate all three vacant *ortho* and *para* positions. An exception is constituted by 3-nitroaniline where only one bromine enters. As with 2- and 4-substituted anilines, the reactivity of the 3-substituted anilines is reduced by the introduction of alkyl groups at the nitrogen atom.

The behaviour of the anilines in the substitution reaction with bromine in medium III-1 should be compared with the analogous reaction between phenols and bromine in the same medium. In this case only one bromine atom enters the ring of a 2-, 3-, or 4-substituted alkylphenol and no reaction takes place if the substituent is deactivating.

CONCLUSIONS

It is concluded that substituted anilines containing halogen or various oxygenated functional groups can be titrated quantitatively with coulometrically generated bromine in water–acetic acid media, with or without added pyridine. The standard titration media are the pyridine-containing media of group I, but in certain instances the pyridine-free medium III-1 should be used. Not all of the investigated anilines can be determined. Thus, trichloroanilines, *p*-iodoaniline and *m*-nitroaniline, although reactive, failed to give quantitative results, while dinitroanilines did not react.

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Table 5. Comparison between reactivity towards bromine for various kinds of anilines in medium III-1

Substituent group	Number of H substituted	Substituent group	Number of H substituted	Substituent group	Number of H substituted
2-Me	2			4-Me	2
N-Me-2-Me	2	3-Me	3	*N*-Me-4-Me	2
N-Et-2-Me	1	*N*-Me-3-Me	2	*N*-Et-4-Me	0
N,*N*-Me_2-2-Me	0	*N*-Et-3-Me	2	*N*,*N*-Me_2-4-Me	0
N,*N*-Et_2-2-Me	0	*N*,*N*-Me_2-3-Me	1	*N*,*N*-Et_2-4-Me	0
2-MeO	2	*N*,*N*-Et_2-3-Me	1	4-MeO	2
2-F	2	3-F	2	4-F	1–2
2-Cl	2	3Cl	2*	4-Cl	~2
2-Br	2	3-Br	~2*	4-Br	~2
2-I	2	3CHO	~2	4-I	~2
2-CHO	1*	3-COOH	~2	*N*,*N*-Me_2-4-CHO	0–1
—	—	*N*,*N*-Me_2-3-COOH	1	4-$COCH_3$	~2
2-COOH	2	3-SO_3H	~2	4-COOH	2
2-COOMe	~2	3-NO_2	~1	4-COOEt	1–2
2-SO_3H	2			4-SO_3H	2
2-NO_2	~1			4-NO_2	1

* Further bromine consumption can be noticed.

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SHORT COMMUNICATIONS

SPECTROPHOTOMETRIC DETERMINATION OF THORIUM WITH XYLENOL ORANGE AND CETYLTRIMETHYLAMMONIUM BROMIDE

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Summary—The thorium–Xylenol Orange reaction sensitized by cetyltrimethylammonium bromide ($\epsilon = 5.51 \times 10^4$ l.mole^{-1}.cm^{-1}) is accompanied by a bathochromic shift from 570 to 600 nm. The system is more selective than the binary system, because the reaction pH is lowered from 4.0 to 2.5; Beer's law is obeyed for 0.04–4.00 ppm of thorium.

The red complex formed by thorium with Xylenol Orange has been used for its spectrophotometric determination,[1] but the method is unselective because of serious interference from rare-earth and other tervalent metals. Mukherji[2] solved the problem of the rare-earths by doing the reaction at pH 2.0 but the procedure lacks sensitivity. The sensitivity has been improved by extracting the Xylenol Orange complex into butanol in the presence of 1,3-diphenylguanidine,[3] but the selectivity is not improved. This communication utilizes the coloured species formed when thorium reacts with Xylenol Orange in the presence of cetyltrimethylammonium bromide (CTAB) in weakly acidic medium. Similar reactions of quaternary ammonium salts with the thorium complexes of Chrome Azurol S,[4,5] Glycinecresol Red[6] and Methylxylenol Blue[7] have already been used for the determination of thorium.

EXPERIMENTAL

Reagents

Thorium solution (500 *ppm*). Dissolve 0.1268 g of $Th(NO_3).6H_2O$ in 100 ml of distilled water containing 1 ml of conc. nitric acid. Dilute to give a 10-ppm solution.

Xylenol Orange solution (0.02%).

Cetyltrimethylammonium bromide solution (0.25%).

Chloroacetic acid buffer, 0.5*M*. Dissolve 12 g of chloroacetic acid in 250 ml of water and adjust to pH 2.5 (pH-meter) with sodium hydroxide.

Procedure

Transfer a sample containing not more than 100 μg of thorium into a 25-ml standard flask. Add, with mixing, 5 ml each of Xylenol Orange solution and chloroacetic acid buffer (pH 2.5) followed by 1 ml of CTAB solution. Dilute to the mark with distilled water and mix. Measure the absorbance at 600 nm in 10-mm cells against distilled water. Establish the concentration by reference to a calibration graph prepared for 10–100 μg of thorium by the procedure above.

RESULTS AND DISCUSSION

Preliminary examination showed that the presence of excess of CTAB was without effect on the red thorium–Xylenol Orange complex, but after systematic investigation it was observed that when a moderate excess of CTAB was used, a blue hue appeared instantaneously upon dilution, the intensity being in direct proportion to the amount of thorium present. An examination of the spectra obtained in the presence and absence of CTAB showed that the absorption maximum of the binary complex at 570 nm shifts to 600 nm in the presence of CTAB; the reagent blank does not absorb at all at this wavelength (Fig. 1). The effects of various experimental parameters on this reaction are shown in Table 1. The amount of thorium used was 20 μg and except for the study of the effect of pH, the solutions were adjusted to pH 2.5 with the chloroacetic acid buffer. Absorbance measurements were made at 600 nm in 10-mm cells after dilution to 25 ml with water. The colour development was instantaneous and the absorbance remained stable for at least 3 hr. The order of addition of reagents has no effect on the absorbance.

Nature of the complex

To find the reacting ratio between thorium and Xylenol Orange the mole-ratio and continuous variation methods were used. The results showed that the ratio of thorium to Xylenol Orange remained 1:2 as in the binary complex.[1] The mole-ratio method was also used to find the reacting ratio between thorium and CTAB in the presence of excess and of stoi-

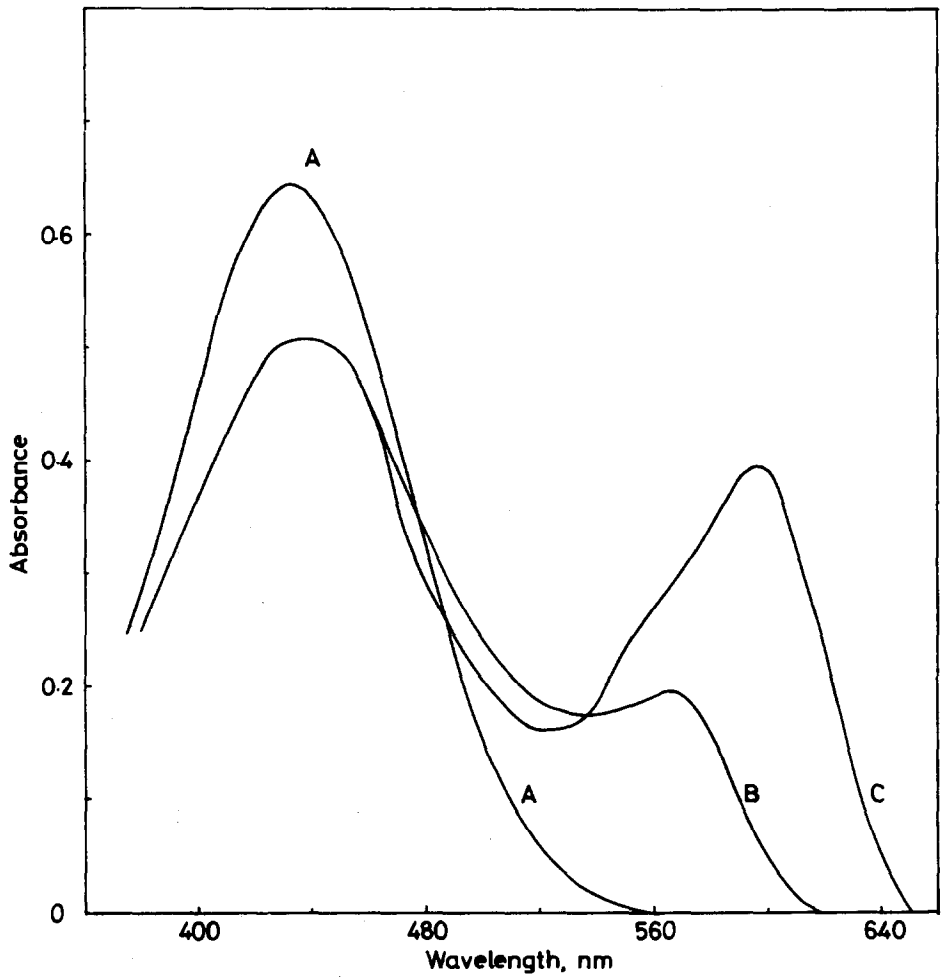

Fig. 1. Absorption spectra of thorium–Xylenol Orange–CTAB system (pH 2.5; total volume 25 ml; 10-mm cells). A, 5.0 ml of 0.02% Xylenol Orange solution with and without CTAB; B, 5.0 ml of 0.02% Xylenol Orange with 40 μg of thorium; C, as in B, with 1.0 ml of 0.25% CTAB solution.

chiometric amounts of Xylenol Orange. The results indicated that at least a 20:1 mole ratio of CTAB to complex is necessary. This suggests that the observed bathochromic shift is due to electrostatic interaction with the CTAB micelles.

Interferences

The recommended procedure was applied to solutions containing 40 μg of thorium and 1-mg amounts of various ions, and the results are summarized in Table 2.

The reduction of Fe(III) and Ce(IV) by ascorbic acid overcomes their interference, and the addition of thiourea eliminates the interference from Cu(II), Pt(IV) and Pd(II). Fluoride can be masked with beryllium prior to addition of the reagents.

Interference from Mo(VI), W(VI), Al, V(V) and phosphate is overcome by co-precipitation of thorium

Table 1. Effect of different parameters on colour reaction (Xylenol Orange and CTAB solutions 2 ml each and pH 2.5, except when varied as shown)

pH	1.5	2.0	2.2	2.5	2.8	3.0	3.5
Absorbance	0.035	0.160	0.175	0.185	0.185	0.175	0.155
Xylenol Orange solution, *ml*	0.5	1.0	2.0	4.0	6.0	8.0	10.0
Absorbance	0.150	0.210	0.200	0.200	0.205	0.170	0.160
CTAB solution, *ml*	0.5	1.0	2.0	2.5	3.0	4.0	5.0
Absorbance	0.060	0.130	0.190	0.190	0.190	0.190	0.165

Table 2. Interference studies

Interferents	Remarks
U(VI), Gd, Sm, La, Nd, Y, Dy, Pr, Ho, Co(II), Mn(II), Ni, Hg(II), Cd, Zn, Fe(II), Pb, Mg, Ca, Ba, Sr, Be, Cr(III), IO_3^-, ClO_4^-, $B_4O_7^{2-}$, AsO_4^{3-}, AsO_3^{3-}, $S_2O_3^{2-}$ (1 mg each); $NaNO_3$, NaCl and Na_2SO_4 (1 mmole each)	No interference
Fe(III), Ti(IV), V(V), Bi, Al, Cr(VI) and U(IV) (1 mg each)	Seriously interfere by increasing the absorbance
Ce(IV), Cu(II), Tl(III), F^-, PO_4^{3-}, citrate, tartrate, EDTA	Seriously interfere by the absorbance
Zr, Hf, W(VI), Mo(VI), Pt(IV), Pd(II) and Sn(II) (1 mg each)	Interfere by precipitating on addition of CTAB

with 1 mg of Fe(III) as the hydrous oxide, by the addition of excess of sodium hydroxide. After centrifuging, the precipitate is washed with 10%sodium nitrate solution and then dissolved in hydrochloric acid. The colour is developed after reduction of Fe(III) with ascorbic acid. No method has been found for removing the interference of Bi, Ti(IV), Zr and Hf, however.

CONCLUSION

The work has shown that the reaction pH of thorium with Xylenol Orange is considerably lowered in the presence of CTAB, with a significant increase in the sensitivity ($\epsilon = 5.51 \times 10^4$ l.mole^{-1}.cm^{-1}) compared with the method of Mukherji[2] ($\epsilon = 2.76 \times 10^4$ l.mole^{-1}.cm^{-1}) and selectivity compared with Otomo's method,[1] though the sensitivity of Otomo's method is higher. The reaction is rapid and the colour stable and reproducible. The method should find application in the analysis of samples such as monazite, as it can tolerate the presence of rare earths and uranium.

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SIMULTANEOUS POLAROGRAPHIC DETERMINATION OF MICRO AMOUNTS OF VANADIUM(V) AND MOLYBDENUM(VI)

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Summary—A simple and sensitive polarographic method has been developed for the determination of micro quantities of vanadium(V) and molybdenum(VI), based on the reduction of bromate, which is catalysed by these metal ions in the presence of 2,4-dihydroxyacetophenone oxime. Interference by various cations and anions has been investigated.

Transition metal ions are known to catalyse the reduction at the dropping mercury electrode of oxidizing agents such as hydrogen peroxide, chlorate, perchlorate, nitrate and hydroxylamine.[1–3] We have studied the effect on bromate. Among the metal ions studied, iron(III),[4] vanadium(V)[5] and molybdenum(VI)[6] were found to exhibit catalytic effects in the concentration range 10^{-3}–$10^{-5}M$. The reduction waves for bromate catalysed by vanadium(V) and molybdenum(VI) occur at 0.0 V and −0.3 V *vs.* SCE respectively. No catalytic wave was detectable at lower molybdenum concentrations (10^{-6}–$10^{-7}M$).

It is also known[7] that organic complexing agents can exert a pronounced influence on catalytic waves. Since resacetophenone oxime (2,4-dihydroxyacetophenone oxime) is known to complex molybdenum(VI)[8] and vanadium(V)[9] in acidic solution, we have studied the effect of this oxime on the reduction of bromate catalysed by vanadium(V) and molybdenum(VI) in the concentration range 10^{-6}–$10^{-7}M$. Addition of the oxime resulted in the appearance of a wave at −0.7 V *vs.* SCE in the case of molybdenum (more negative by about 0.4 V than the one obtained at high molybdenum concentrations in the absence of the oxime), though no significant change was noticed in the case of the vanadium wave. This fact has been exploited to develop a simple and sensitive polarographic method for the simultaneous determination of micro amounts of vanadium and molybdenum.

EXPERIMENTAL

All chemicals used were of analytical-reagent grade. Stock solutions of ammonium metavanadate ($5 \times 10^{-5}M$), ammonium molybdate ($1 \times 10^{-5}M$) and mixtures of the two, prepared in conductivity water, were used in the

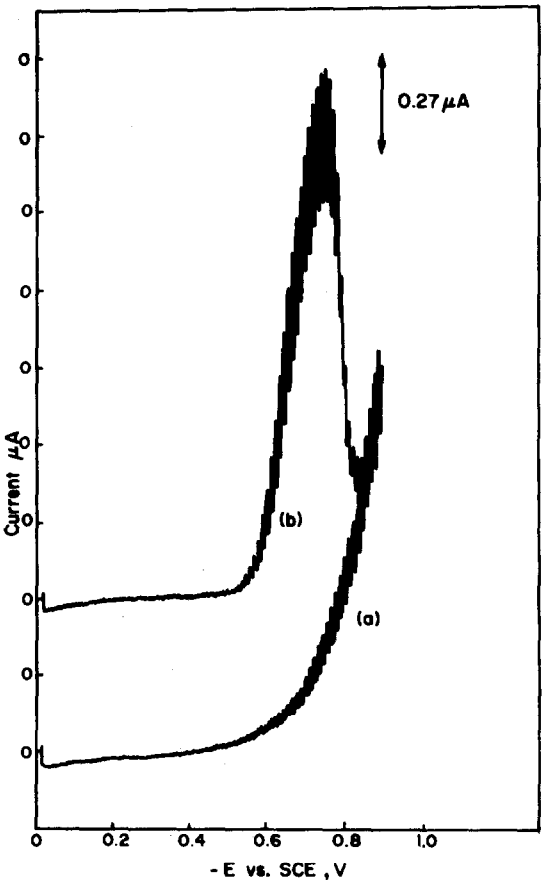

Fig. 1. (a) Polarogram of molybdenum(VI) + bromate in acetate–acetic acid buffer (pH 5.0), $[Mo(VI)] = 20 \times 10^{-7}M$, $[BrO_3^-] = 5 \times 10^{-2}M$. (b) Polarogram of molybdenum(VI) + bromate + oxime in acetate–acetic acid buffer (pH 5.0), $[Mo(VI)] = 20 \times 10^{-7}M$, $[BrO_3^-] = 5 \times 10^{-2}M$, [oxime] $= 4 \times 10^{-4}M$.

studies. There was no visible change in the solutions, nor did the height of their polarographic waves change, on storage of the solutions for 48 hr.

A recording polarograph, a Lingane-type H-cell and a digital pH-meter were used in the studies.

Procedure

To different aliquots of the mixed stock solution of molybdenum and vanadium, in a 25-ml standard flask, were added 5 ml of bromate solution (0.25*M*) and 1 ml of the oxime solution (0.01*M*), and the contents were made up to the mark with a sodium acetate–acetic acid buffer solution of pH 5.0. After mixing, some solution was transferred to the polarographic cell. Pure nitrogen gas was bubbled through for about 10 min to remove dissolved oxygen, and the current–voltage curves were recorded.

RESULTS AND DISCUSSION

Typical polarograms are presented in Figs. 1–3. From curves 1(a) and 1(b), it is seen that at low concentrations of molybdenum (10^{-6}–$10^{-7}M$) a wave with a sharp maximum is obtained at −0.7 V *vs.* SCE in the presence of the oxime. The curves 2(a) and 2(b) on the other hand reveal that the reduction wave occurs at zero applied voltage at low concentrations of vanadium even in the absence of the oxime and that there is no significant change in the shape of the wave on addition of the oxime. It is also clear from the curve in Fig. 3 that the shapes and positions of the waves 1(b) and 2(b) are not affected by the simultaneous presence of molybdenum(VI) and vanadium(V). Polarograms of the mixed solutions containing different amounts of the metal ions were recorded by the procedure described, and the currents corresponding to the peaks were measured. The linear plots that were obtained when peak-height was plotted against concentration over the ranges 4–16 × $10^{-6}M$ for vanadium and 4–24 × $10^{-7}M$ for molybdenum suggested the possibility of using this method for the simultaneous determination of micro amounts of the two metals. Polarograms recorded in the presence of 1000-fold amounts of iron(III), cobalt(II), nickel, zinc, magnesium, calcium, tungsten(VI), cadmium, copper and lead revealed that iron, cobalt, nickel, zinc, magnesium and calcium did not interfere in the determination. Copper was precipitated as the oximate complex under the experimental conditions and interfered. Cadmium and lead were reduced at −0.63 and −0.45 V *vs.* SCE respectively in the medium used, and interfered since their waves pre-

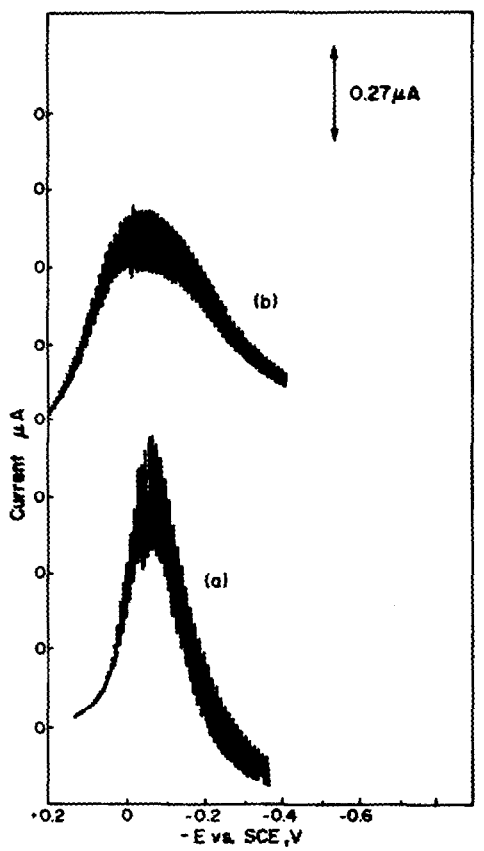

Fig. 2. (a) Polarogram of vanadium(V) + bromate in acetate–acetic acid buffer (pH 5.0) [V(V)] = 8 × $10^{-6}M$ [BrO_3^-] = 5 × $10^{-2}M$. (b) Vanadium(V) + bromate + oxime in acetate–acetic acid buffer (pH 5.0) [V(V)] = 8 × $10^{-6}M$ [BrO_3^-] = 5 × $10^{-2}M$ [Oxime] = 4 × $10^{-4}M$.

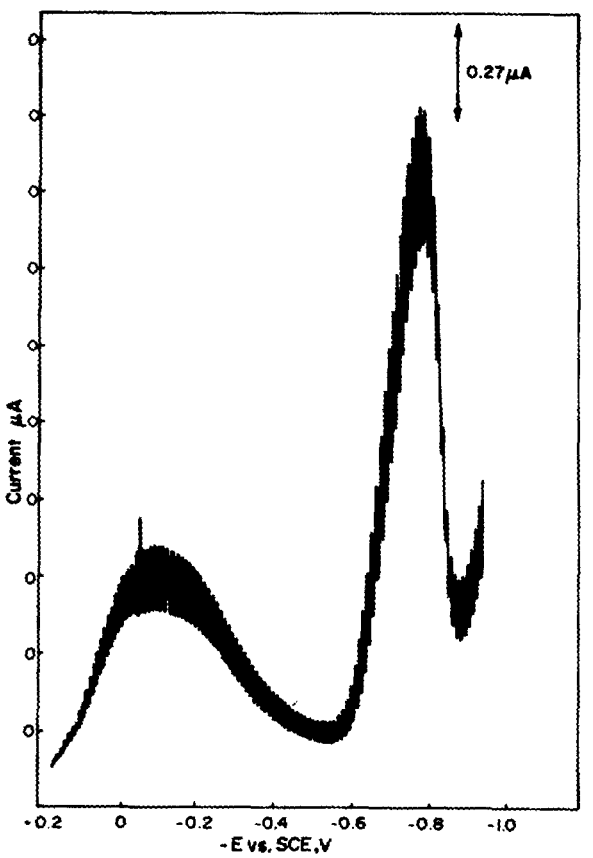

Fig. 3. Polarogram of vanadium(V) + molybdenum(VI) + bromate + oxime in acetate–acetic acid buffer (pH 5.0). [V(V)] = 8 × $10^{-6}M$ [Mo(VI)] = 20 × $10^{-7}M$ [BrO_3^-] = 5 × $10^{-2}M$ [Oxime] = 4 × $10^{-4}M$.

ceded the catalytic waves. Tungsten completely suppressed the vanadium wave. The standard deviations calculated for the vanadium and molybdenum catalytic peaks were 0.003 and 0.002 μA respectively.

The results thus confirm that Mo(VI) and V(V) at low concentrations can be determined simultaneously by the polarographic method described. In the absence of bromate and oxime, only very small limiting currents were recorded for these metals, and further, the limiting currents did not vary linearly with the concentration of the metal ion.

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ANALYTICAL DATA

STABILITY CONSTANTS AND MOLAR ABSORPTIVITIES FOR COMPLEXES OF CHROMIUM(III) AND COBALT(II) WITH 2-PYRIDYLMETHANAMINE

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Summary—The stability constants and molar absorptivities of complexes of Cr^{3+} and Co^{2+} with 2-pyridinemethanamine have been determined from spectrophotometric data of very dilute aqueous solutions.

Several investigators[1-7] have reported equilibrium constants for complexes of metal ions with 2-pyridylmethanamine (2-aminomethylpyridine; 2-picolylamine; L), but have given no molar absorptivities; the formation constants for Cr^{3+} with L have also not been reported. We have determined the stepwise stability constants and the molar absorptivities (ϵ, $l.mole^{-1}.cm^{-1}$) for complex ions of Cr^{3+} and Co^{2+} with 2-pyridylmethanamine.

EXPERIMENTAL

Apparatus and measurements

A Cary Model 17 spectrophotometer was used to record precise absorbance measurements with solutions at 25°.

Reagents

The 2-pyridylmethanamine was obtained from the Aldrich Chemical Company. The metal ion solutions were prepared from G. Frederick Smith Chemical Company $Cr(ClO_4)_3.6H_2O$ and $Co(ClO_4)_2.6H_2O$ reagents. Ligand and metal ion solutions were standardized by conventional methods.

Procedure

Spectrophotometric data were obtained from freshly prepared solutions. Separate aqueous stock solutions containing ligand and metal ion were prepared. Portions of the stock solutions were mixed with water for dilution to prepare a series of solutions that were 0.1–0.8m*M* in Cr^{3+} and 0.2–5.0m*M* in ligand, and another series that was 0.05–0.8m*M* in Co^{2+} and 0.025–1.5m*M* in ligand. The solutions were mixed well, and absorption spectra were obtained as soon as possible after the mixing. No salt was added to raise the ionic strength; thus, our solutions were typically at very low ionic strengths (0.15–3.0m*M*). Approximately fifty solutions were prepared and many spectra were obtained.

Calculations

Stability constants and molar absorptivities at five wavelengths for Cr^{3+} and four wavelengths for Co^{2+} complexes were calculated with the computer program of Lingane.[8]

RESULTS AND DISCUSSION

The results are given in Tables 1–3. Our values for the stability constants and molar absorptivities of complexes of Cr^{3+} with the ligand are given in Table 1, and our stability constants for complexes of Co^{2+} with the ligand are given in Table 2 along with previously reported results.[1-6] Our values of molar absorptivities for complexes of Co^{2+} with the ligand are given in Table 3.

As seen from Table 2, the stability constants obtained for complexes of Co^{2+} with 2-pyridylmethanamine by various investigators are in fairly close agreement. Goldberg and Fernelius[1] used pH titrations, with solutions of low ionic strength, and the results given in Table 2 are for 20°, calculated to zero ionic strength. Holmes and Jones[2] used potentio-

Table 1. Values of stability constants and molar absorptivities for complexes of Cr^{3+} with the ligand

Stability constants			Molar absorptivities, $l.mole^{-1}.cm^{-1}$				
			350 nm	400 nm	500 nm	600 nm	700 nm
		ϵ_{Cr}	4	11	5	11	1
$\log K_1$	5.65	ϵ_{CrL}	73	43	33	22	0.02
$\log K_2$	3.16	ϵ_{CrL_2}	650	759	403	253	187
$\log K_3$	2.21	ϵ_{CrL_3}	383	109	148	141	126
		ϵ_L	0	0	0	0	0

Table 2. Values of stability constants for complexes of Co^{2+} with the ligand

	This study	Goldberg and Fernelius[1]	Holmes and Jones[2]	Lane and Thompson[3]	Lacoste and Martell[4]	Anderegg[5]	Goeminne and Eeckhaut[6]
log K_1	5.62	5.51	≃5.8	5.75	5.3	5.68	5.54
log K_2	5.02	4.70	—	4.58	—	4.70	4.79
log K_3	4.26	3.45	—	(2.80)	—	3.60	3.50

Table 3. Values of molar absorptivities for complexes of Co^{2+} with the ligand

	Molar absorptivities, $l.mole^{-1}.cm^{-1}$			
	450 nm	500 nm	550 nm	600 nm
ϵ_{Co}	0	0	0	0
$\epsilon_{Col.}$	192	196	191	183
$\epsilon_{Col._2}$	184	173	166	162
$\epsilon_{Col._3}$	352	302	278	267
ϵ_{L}	0	0	0	0

metric titrations at 25° with solutions of ionic strength 0.01–0.02 and reported a value only for log K_1. Lane and Thompson[3] derived results from potentiometric titrations at 25° in 50% v/v aqueous dioxan solutions. Lacoste and Martell[4] reported only log K_1 from potentiometric titrations of solutions at ionic strength 0.1 and at 25°. Anderegg[5] made potentiometric measurements at 20° with solutions of 0.1 ionic strength. Goeminne and Eeckhaut[6] obtained constants from potentiometric data at 25° in 0.5*M* potassium nitrate media. The use of temperatures of 20° or 25° and water or a 50% dioxan/water solvent mixture seems to make little difference in the log *K* values. Our spectrophotometric data seem to give somewhat higher results for log K_2 and log K_3, which is in agreement with a spectrophotometric study by Hseu and Tsai.[7] For solutions at 25° and ionic strength of 0.1, they found log $\beta_2 = 10.62$ ($\beta_2 = K_1K_2$), which agrees well with log $\beta_2 = 10.64$ calculated from our results in Table 2.

Experience in our laboratory with this reagent and with these metal ions has shown that the reactions are rapid and quantitative; and although the molar absorptivities are somewhat low, the reactions can be used for photometric titrations with an instrument with electronic scale-expansion capabilities, such as the Cary Model 17 spectrophotometer. With a less sophisticated instrument, photometric titrations should be feasible with 5 or 10-cm cuvettes. The important points are that the reactions proceed rapidly and with definite fixed reaction stoichiometry, permitting fast and accurate quantitative analyses.

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ANNOTATION

METAL CHELATES OF PHOSPHONATE-CONTAINING LIGANDS—I

STABILITY OF SOME *N,N,N',N'*-ETHYLENEDIAMINETETRA(METHYLENEPHOSPHONIC) ACID METAL CHELATES

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Summary—A potentiometric investigation of the acid dissociation constants of the octabasic ENTMP [*N,N,N',N'*-ethylenediaminetetra(methylenephosphonic) acid] is reported. The stability constants of protonated MH_nL (n = 1, 2, 3 and 4) and unprotonated ML metal chelates of Mg, Ca, Ba and Cd with ENTMP have been measured. The stabilities are in the order Mg < Ca < Ba < Cd.

Organic phosphonates form a very attractive and effective class of substance for inhibiting calcification. ENTMP, *N,N,N',N'*-ethylenediaminetetra(methylenephosphonic) acid has been shown to be extremely effective, even at concentrations as low as $10^{-6}M$, in preventing the precipitation or the dissolution of calcium phosphate,[1] sulphate[2] and carbonate[3] or barium sulphate,[4] and the dehydration of calcium oxalate.[5] In addition, small quantities of methylenediphosphonate can prevent ^{45}Ca and $H^{32}PO_4^{2-}$ exchange from a calcified organic matrix,[6] indicating that an unusually stable association is taking place between the inhibitor and the calcium and/or the phosphate ions present at the surface of the calcified material.

Very few equilibrium data on this ligand have been reported,[7-8] and the values of the equilibrium constants published differ greatly, even for identical systems. It is the purpose of the present paper to investigate the formation of the magnesium, calcium, barium and cadmium complexes of ENTMP.

EXPERIMENTAL

Reagents

Pure recrystallized tetrasodium salt, Na_4H_4ENTMP was kindly donated by Unilever Research Laboratories, Port Sunlight, U.K. The purity was nearly 100% as measured by potentiometric titration with standard sodium hydroxide.

Stock solutions of metal nitrates were standardized with EDTA, and diluted as required.

All reagents were analytical grade materials.

Apparatus

An Orion Research Digital Ionalyzer, Model 801A, fitted with a combined glass calomel electrode type 91-04, was used.

Procedure

ENTMP, acidified with nitric acid, was titrated potentiometrically at 25° with standard sodium hydroxide solution in the absence and presence of magnesium, calcium, barium and cadmium ions at 1:1 and 1:2 molar ratios of metal to ligand. The concentration of the ligand was approximately $1 \times 10^{-3}M$ and the volume of the experimental solution was 25 ml. The ionic strength was maintained at 0.1 with potassium nitrate.

Calculations

In the mathematical treatment, the following notations are used: C_L = total analytical concentration of ligand; C_M = total analytical concentration of metal ion; C_H = total bound and free hydrogen ion concentration; C_{OH} = total molar concentration of base added to the experimental solution; a = number of moles of base added per mole of ligand; K_n = protonation constant of the ligand ($K_n = [H_nL]/[H]\,[H_{n-1}L]$); $K^M_{MH_nL}$ = formation constant of complex MH_nL, ($K^M_{MH_nL} = MH_nL]/[M]\,[H_nL]$).

For calculating the hydrogen ion concentration from pH measurements, $f_\pm$ was taken as 0.769 at $I = 0.1$.

Protonation constants. The protonation constants of the ENTMP were calculated by Schwarzenbach's graphical method[9] with a small modification based on the assumption that the number of protonated species dominant within a buffer region is restricted.

In the first dissociation step, where $0 < a < 2$ and $[H^+] \gg [OH^-]$, the values of K_7 and K_8 can be obtained from the equation

$$\frac{1}{K_8} = \frac{[H]\{aC_L + [H]\}}{\{(2-a)/[H]C_L - 1\}} K_7 + \frac{\{(a-1)C_L + [H]\}}{\{(2-a)/[H]C_L - 1\}} \quad (1)$$

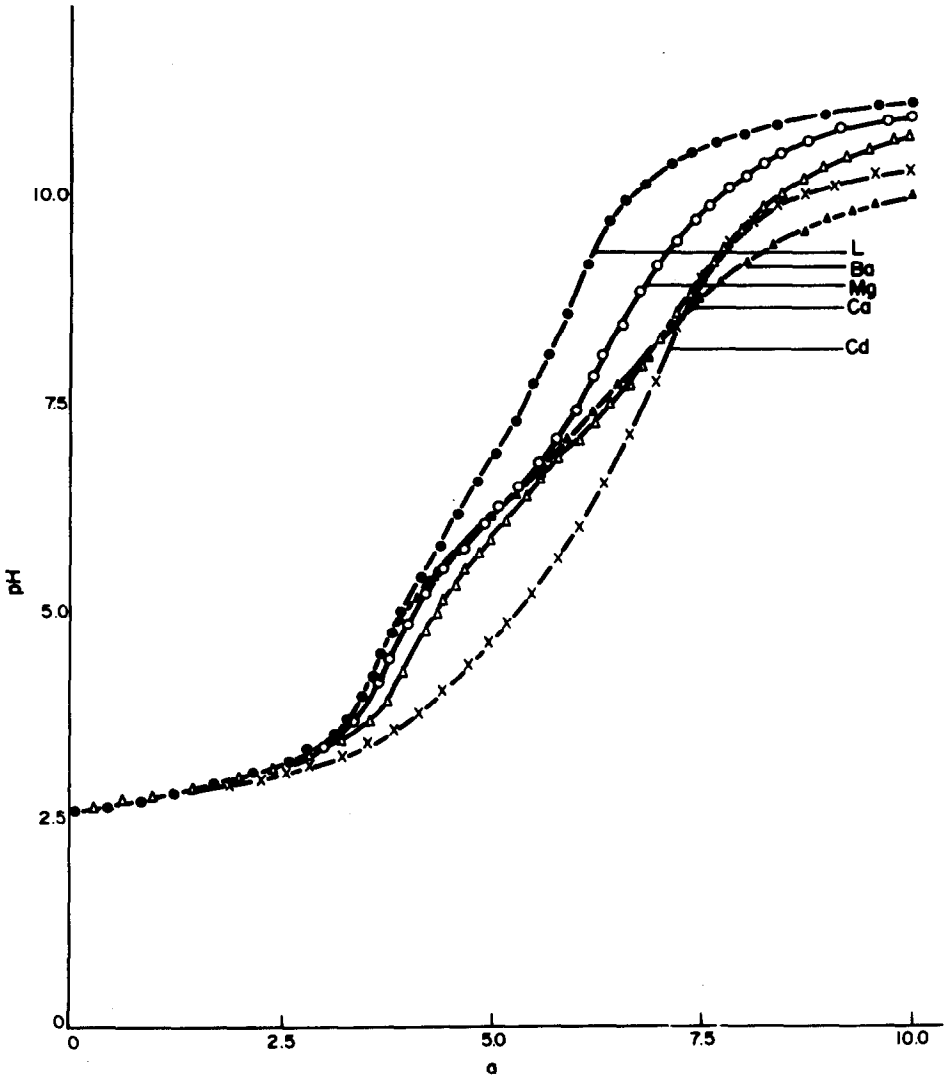

Fig. 1. Potentiometric titration curves of Mg, Ca, Ba and Cd ions with ENTMP for 1:1 mole ratio of metal to ligand at 25°, $I = 0.1$ (KNO_3).
L = Free ligand; a = moles of base added per mole of ENTMP.

This corresponds to:

$$\frac{1}{K_8} = \frac{B}{A} K_7 + B \tag{2}$$

If A and B are calculated, the set of straight lines drawn through corresponding values of A and B will all intersect at one point, the co-ordinates of which are $1/K_8$ and K_7.

Similar equations were derived for the buffer regions $2 < a < 4$; $4 < a < 6$ and $6 < a < 8$ to obtain K_n (where $n = 6, 5, 4, 3, 2$ and 1).

Stability constants of the MH_nL *species.* The formation function, $\bar{n}$, and the free ligand concentration were calculated by using a modified version of the method of Carlson *et al.*[10] These values were obtained by using a small FORTRAN IV program run on a Nova 830 mini-computer. The two expressions which can be readily deduced from the mass-balance for total metal (C_M) and total ligand (C_L) and the electroneutrality condition, are:

$$\bar{n} = \left(C_L - \frac{C_H - [H]}{\bar{n}_H} \right) \Big/ C_M \tag{3}$$

and

$$[L] = \frac{\alpha}{\bar{n}_H} (C_H - [H]) \tag{4}$$

where α is the fraction of the ligand that is in free unprotonated form and $\bar{n}_H$ is the average number of hydrogen ions bound per ion of free ligand:

$$\alpha = 1/(1 + K_1[H] + K_1K_2[H]^2 + \ldots) \tag{5}$$

and

$$\bar{n}_H = \frac{K_1[H] + 2K_1K_2[H]^2 + \ldots}{1 + K_1[H] + K_1K_2[H]^2 + \ldots} \tag{6}$$

Equation (3) can be rearranged as a function of the protonation constants, the stability constants of the

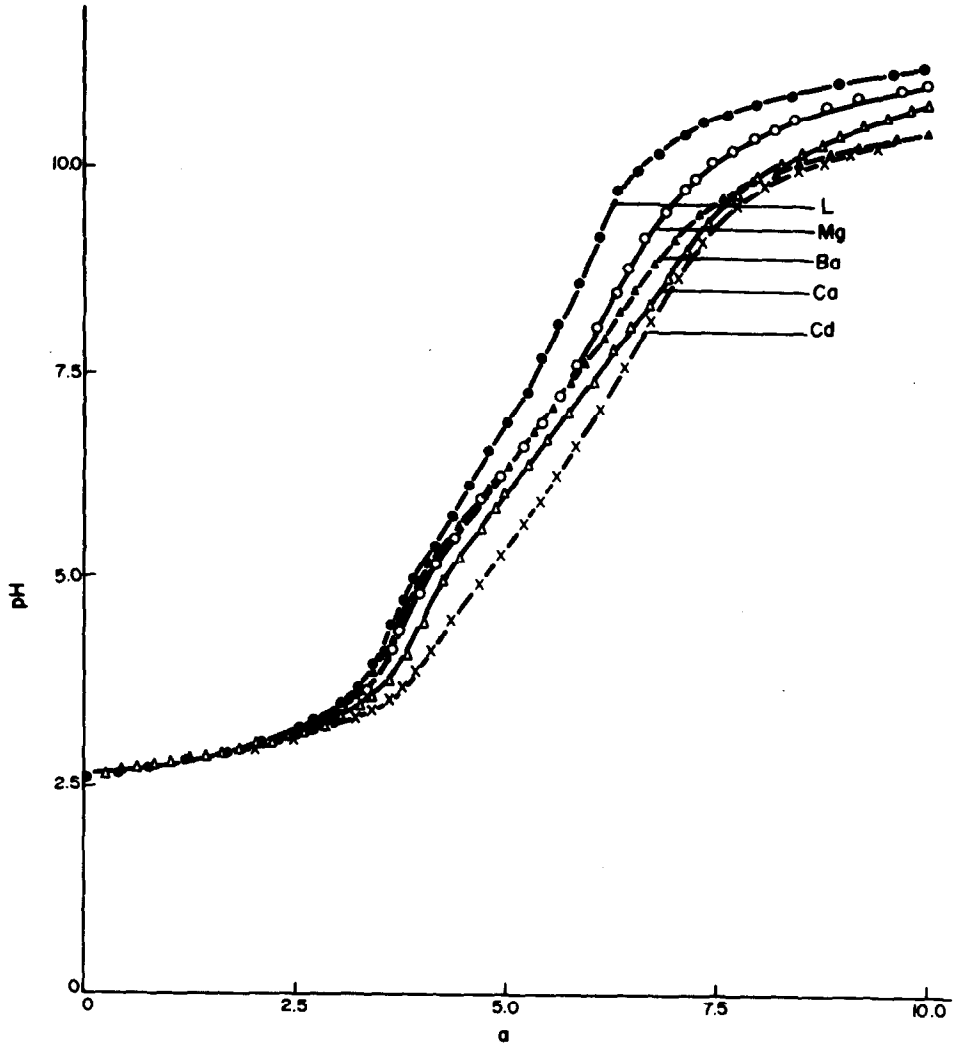

Fig. 2. Potentiometric titration curves of Mg, Ca, Ba and Cd ions with ENTMP for a 1:2 mole ratio of metal to ligand at 25°, $I = 0.1$ (KNO_3).

complex species, and the free ligand and hydrogen ion concentrations:

$$\frac{\bar{n}}{(1-\bar{n})[L]} = K^{M}_{ML} + K^{M}_{MHL} K_1[H] + K^{M}_{MH_2L} K_1 K_2 [H]^2 + \ldots \quad (7)$$

The values of $K^{M}_{MH_nL}$ were then obtained by graphical solutions to equation (7) for the different pH regions where the complex species MH_nL were assumed to predominate.

RESULTS AND DISCUSSION

Potentiometric titration curves of 1:1 and 1:2 molar ratios of Mg, Ca, Ba and Cd ions to ENTMP are shown in Figs. 1 and 2. Figure 1a is the titration curve for the acidified ligand in absence of metal ions.

Table 1 lists the values of the protonation constants obtained from the present work as well as those published previously.[7,8] In order to check and compare these values, the average numbers of protons bound to the ligand, $\bar{n}_H$ were calculated from experimentally

Table 1. Protonation constants of ENTMP (25°, $I = 0.1$, KNO_3)

	log K_1	log K_2	log K_3	log K_4	log K_5	log K_6	log K_7	log K_8
Present work	10.60	10.48	9.27	7.39	5.63	3.80	2.73	2.43
Ref. 7	10.60	9.22	7.43	6.63	6.18	5.05	2.72	1.46
Ref. 8	12.10	10.18	8.08	6.54	5.23	3.00	—	—

Table 2. Values of $\bar{n}_H$ calculated from equations (8) and (6) with different values of K_n

a	$\bar{n}_H$ calculated by equation (8)	$\bar{n}_H$ calculated by equation (6) and our values of K_n	$\bar{n}_H$ calculated by equation (6) and K_n values in Ref. 7	$\bar{n}_H$ calculated by equation (6) and K_n values in Ref. 8
1.186	5.58	6.43	6.38	5.53
2.964	5.02	4.98	5.65	4.76
3.952	4.05	4.04	3.74	3.59
4.940	3.06	3.05	2.07	2.44
5.928	2.15	2.03	1.09	1.73
6.718	1.52	1.48	0.77	1.45
7.311	1.07	1.17	0.63	1.33

measured quantities by using the equation

$$\bar{n}_H = \frac{(8 - a)C_L + [OH] - [H]}{C_L} \quad (8)$$

These were then compared with the corresponding values calculated as a function of the hydrogen ion concentration and of the protonation constants [equation (6)].

Both values agreed very closely, whereas results obtained by using literature values of K_n showed marked discrepancy. A sample of these calculations is given in Table 2.

It is evident from Figs. 1 and 2 that the stability sequence is in the order Mg < Ca < Ba < Cd and the complex formation with the completely deprotonated form is incomplete at pH < 9–10. Appreciable complex formation is obvious in the case of Cd at $a = 4$ and with Ca, Mg and Ba at $a = 5$, which suggests the presence of protonated species. All the curves are characterized by two inflections, the position of which is dependent upon the metal ion. The equilibrium constants calculated for the systems studied are given in Table 3.

It is worth noting that the trend of stability order given above is different from that obtained with other complexing agents, such as EDTA,[9,11] DCTA,[11] and DTPA,[12] and the values of log K are lower than those for any hexadentate ligand. This is in agreement with the conclusions of Westerback *et al.*[7] who attribute the low stability of these chelates to the large negative charges of the phosphonate groups preventing them from all coming together about a single positively charged metal ion.

The greater stability of the barium complex compared with those of calcium and magnesium is probably due to the greater size of the barium ion, which reduces the repulsion forces in the phosphonate chelate by expansion of the chelate ring.

Table 3. Formation constants of ENTMP with magnesium, calcium, barium and cadmium ions at 25°, I = 0.1 (KNO_3)

M^{2+}	Log $K^M_{MH_nL}$				
	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
Mg^{2+}	4.78	4.03	3.45	3.06	—
Ca^{2+}	6.34	4.48	3.85	3.22	—
Ba^{2+}	7.88	6.95	4.31	3.53	—
Cd^{2+}	9.18	7.41	4.86	4.14	3.60

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STUDY OF A GLASSY CARBON ELECTRODE IN AMPEROMETRIC DETECTION USING d.c., NORMAL AND DIFFERENTIAL PULSE TECHNIQUES

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Summary—The results of a comparative study on d.c., normal pulse and differential pulse techniques applied to anodic amperometric detection at a glassy carbon electrode in a voltammetric flow-through cell are presented. The important aspects examined are response time, linearity, limit of detection and selectivity. It is shown that the d.c. mode is the most favourable as long as no adsorption of oxidation products takes place. If strong adsorption occurs, normal pulse detection is recommended, although the limit of detection is somewhat larger.

In recent years, much attention has been paid to the potentialities of electrochemical methods of detection in high-performance liquid chromatography (HPLC). A review article on the use of voltammetric and coulometric cells for liquid chromatography, including mention of electrode materials, was recently published by Kissinger.[1] In a coulometric cell, designed by Takata and Muto,[2] so-called carbon cloth was used as the working electrode. The material seems to consist of glassy carbon fibres. The cell was used for the direct and indirect coulometric detection of various species such as metal ions, inorganic anions, organic acids, phenols and sugar. Lankelma and Poppe[3] have described a coulometric detector consisting of two parallel flat glassy carbon electrodes. The applicability to this detector to the detection of biogenic amines was investigated by Tjaden *et al.*[4] Amperometric detection (d.c. mode) with carbon paste electrodes was applied by Kissinger *et al.*[1] to a large number of analytical problems.

Some information on the use of different polarographic techniques in flow-through cells is also available. MacDonald and Duke[5] have published a preliminary evaluation of use of pulse techniques in combination with platinum and carbon electrodes. Normal pulse and a.c. techniques were examined by Fleet and Little,[6] using a glassy carbon wall-jet electrode as well as a dropping mercury electrode. Swartzfager[7] compared d.c., normal and differential pulse voltammetry, using a carbon paste electrode.

In this paper the results are given of a comparative study of d.c., normal and differential pulse techniques in amperometric detection at a glassy carbon electrode. The important aspects that have been examined are response time, linearity, limit of detection and selectivity. Some attention has also been paid to the influence of adsorption phenomena at the electrode surface.

EXPERIMENTAL

The detector used in our experiments is shown in Fig. 1. The cell block is made of "Perspex". The cell has an inner diameter of 3 mm and a thickness of 1 mm, which results in a cell volume of 8 μl. A glassy carbon rod, 3 mm in diameter (GC-20 Tokai Electrode Manufacturing Co. Ltd, Tokyo) was mounted in a "Teflon" holder and used as the working electrode. Electrical contact was made by means of a small amount of mercury inside the tube and a brass screw at the top of the electrode holder. The reference electrode was a silver wire anodically covered with silver chloride. With constant chloride concentration level in the eluent, a stable reference potential was observed. The stainless-steel "Swagelok" connector in the outlet of the "Perspex" cell was used as the auxiliary electrode. All experiments were carried out with a PAR 174 polarographic analyser. Current–time relations were recorded with a Servogor RE 541. An Omnigraphic X–Y recorder (Houston Instrument) was used in the adjustment of the indication potential in the normal pulse mode. The time between two successive pulses was set at 0.5 sec for normal and differential pulses throughout the experiments. The flow was effected either hydrostatically or by means of a peristaltic pump (Gilson Minipuls 2). The inner diameter of the "Teflon" tubes was 0.8 mm and they were connected with zero dead-volume connectors (Pierce "Chromatoflo"). An injection port was used as well as a sample loop (sample injection slide-valve, Pierce "Chromatoflo"). To check the appropriate indication potential the peak currents obtained after injections of equal amounts of samples were recorded as a function of potential. Finally, the detector was tested in combination with a chromatographic system.[8]

In all experiments distilled water was used. The $10^{-4}M$ potassium hexacyanoferrate(II) solution was freshly prepared before use by diluting a $10^{-1}M$ stock solution in 0.2% sodium carbonate and stored in a dark-coloured bottle, because more dilute solutions are light-sensitive.[9] The metol (*p*-methylaminophenol sulphate) solution was also freshly prepared before use. All chemicals used were of analytical grade.

Chromatographic conditions

The chromatographic experiments were carried out with a high-pressure liquid chromatograph (1010 A LC, Hew-

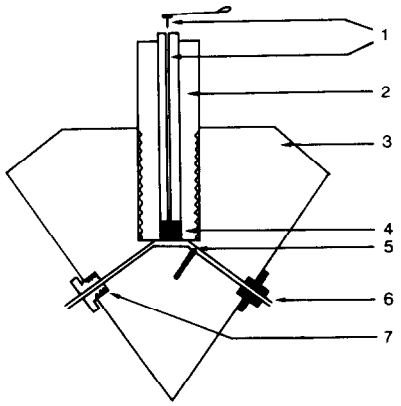

Fig. 1. Electrochemical flow-through cell. 1, Brass screws; 2, "Teflon" holder; 3, "Perspex" box; 4, glassy carbon electrode; 5, reference electrode (Ag/AgCl); 6, outlet with Swagelok connector (auxiliary electrode); 7, inlet.

lett-Packard), a high-pressure sampling valve (Valco CV-6-UHpa) and a thermostatically controlled (25°) stainless-steel column 250 mm long and 2.8 mm in bore fed by a thermostatic water-bath (Haake NB 22). The wavelength for the ultraviolet detection was adjusted to 280 nm. The column materials used were commercially available octyl-modified silica (Rp-8, mean particle size 5 or 10 μm, Merck, Darmstadt, GFR) loaded with SDS (sodium dodecylsulphate). Mobile phase: 0.02M sodium citrate (pH = 2.0) + 3% v/v propan-1-ol + 0.02M sodium perchlorate + 0.001% w/v SDS.

RESULTS AND DISCUSSION

Response time

The response time was measured by means of a stepwise response experiment. The detector was connected to two large bottles by means of a three-way cock, immediately before the detector. One bottle was filled with 0.05M potassium chloride and the other with $10^{-4}M$ potassium hexacyanoferrate(II) in 0.05M potassium chloride. Hexacyanoferrate(II) was chosen because it shows reversible electrode behaviour at the glassy carbon electrode. Switching the cock from one position to the other causes the concentration profile for the hexacyanoferrate(II) applied to the electrode to be stepwise in nature. The resulting current was recorded. The indication potential was +0.7 V in both the d.c. and normal pulse modes, with a rest potential of +0.2 V for the latter. In the differential pulse mode the potential was set to +0.55 V and a pulse amplitude of 100 mV was chosen.

For characterization of the response time curves, the time needed to reach 90% of the maximum signal (t_{90}) and the delay time (t_d) (due to the dead volume between cock and cell) are important (Fig. 2). The values observed for t_{90} and t_d are represented in Fig. 3. The response times can depend on both the electrochemical cell and on the different modes in which the instrument is used. The instruction manual for the instrument[10] gives little information about the response time. The instrumental response in the d.c. mode is said to be fast relative to the response time of any recorder. For the normal pulse mode the "time constant" is given as the duration of one sampling, *i.e.*, 16.7 msec, but in our opinion the response time in the pulse mode should also be related to the time between two successive pulses.

According to the manual, for the differential pulse mode 25 current-sample pairs are needed before the current is within 1% of the final value. To reach 90% of the final signal a response time (t_{90}) of 16 current-sample pairs (8 sec) was found necessary by means of a simulation experiment. This is in close agreement with the results in Fig. 3 for flow-rates larger than about 1 ml/min and means that at these flow-rates the instrumental response time of the PAR system in the differential pulse mode is larger than the response time of the detector cell, resulting in an extra broadening of the recorded peaks.

In the normal pulse mode, two current-samples (about 1 sec) are needed to reach within 10% of the final value. In the d.c. mode, the instrumental response time is even shorter. This implies that in the latter two modes, the response time found experimentally can be attributed to the detector. The relatively large values might be partly caused by the dead volume (17 μl) between injection port and cell; a reduction of this dead volume would then lead to a decrease in the experimental response times and allow a better differentiation between the d.c. and normal pulse modes. However, this experiment indicates the order of the response times for the three instrumental modes.

The dependence of the current on the flow-rate

The flow-rate studies were carried out by pumping through the cell a solution containing metol as the electroactive material. Metol was chosen instead of hexacyanoferrate(II) because we were especially interested in organic compounds. A solution of metol became purple after standing overnight. This was

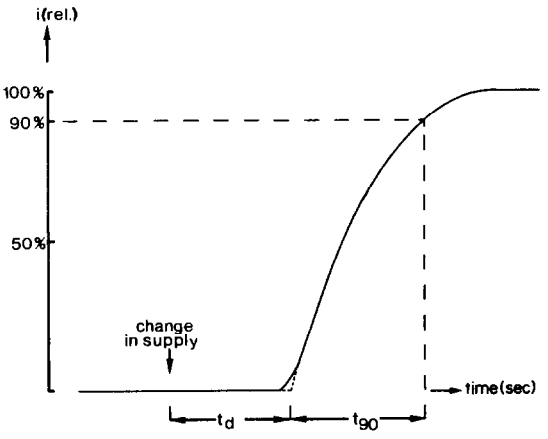

Fig. 2. Schematic current–time curve after application of concentration step.

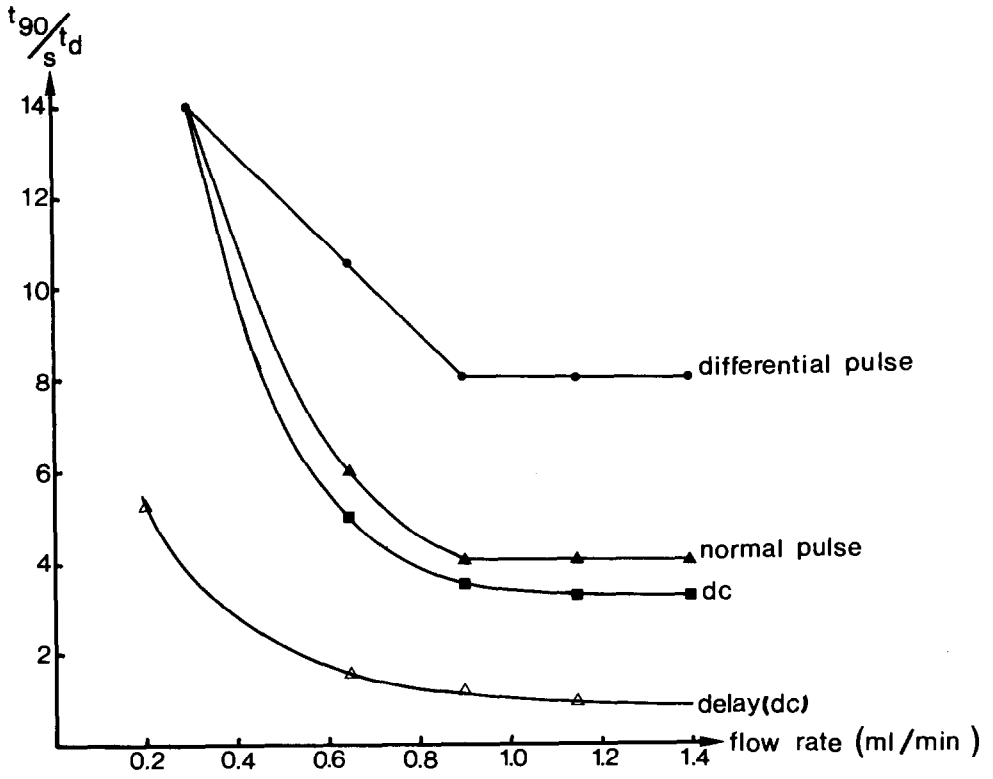

Fig. 3. Measured response times *vs.* flow-rate in the three modes, and the delay in the d.c. mode.

caused by oxidation–polymerization reactions. The differential pulse voltammogram obtained with such a coloured solution differs from that obtained with a colourless solution. Therefore, freshly prepared metol solutions were used in the further experiments. A log–log plot of the current (observed at a potential of +0.6 V) *vs.* the flow-rate shows that $i \propto \langle v \rangle^{1/2}$, where $\langle v \rangle$ denotes the mean linear flow-rate.

In the normal pulse mode the current was found to be nearly independent of the flow-rate, the relative standard deviation of the current being 2%. Similar behaviour was observed in the differential pulse mode (rel. std. devn. 1.5%). These results for the normal and differential pulse modes are about the same as those found by Swartzfager[7] with a carbon paste electrode.

Linearity

The linearity of the detector was tested with 180-μl samples of metol solutions. For the d.c. mode a linear relationship was obtained in the concentration range 6×10^{-4}–$6 \times 10^{-8} M$ (100–0.01 nmole). For the normal pulse mode a linear relationship was observed in the concentration range 8×10^{-5}–$1 \times 10^{-6} M$

Table 1. Static noise of the detector in the d.c., pulse and differential pulse modes

Integration time, *sec*	Detection mode	Standard deviation of the current, *nA* a^*	b^*
1	d.c.	0.10	0.09
10	d.c.	0.08	0.15
	normal pulse	0.34	0.33
	diff. pulse	0.46	0.25
50	d.c.	0.04	0.13
	normal pulse	0.35	0.35
	diff. pulse	0.46	0.24

Conditions: potential working electrode +0.60 V in d.c. and normal pulse (rest potential +0.10 V) modes; in the differential pulse mode the potential was +0.275 V and the amplitude 100 mV. Eluent 0.05*M* KCl. Flow-rate 0.70 ml/min.

*a** with "Minipuls" pump.

*b** syphoned hydrostatically.

(15–0.2 nmole), whereas a small deviation from linearity for the same concentration range was observed for the differential pulse mode. This deviation might be caused by the small shifts in the peak potential of the differential pulse voltammograms. The reason for the smaller concentration range found for the normal and differential pulse methods as compared with d.c., will be given in the next section.

The dependence of the peak current, in the differential pulse mode, on the amplitude was tested under static conditions by injecting large samples (0.5 ml) of solutions of metol. The indication potential, E_p, was calculated from $E_p = E_{1/2} - \Delta E/2$,[11] where ΔE denotes the pulse amplitude. The peak currents increase linearly with the amplitude up to 100 mV. A similar relationship was obtained for quiescent metol solutions. The peak currents have been corrected for the large residual currents.[12]

Noise and limit of detection

For the detector to be applicable in chromatography, it is necessary to have a sufficiently constant base-line. To assess the order of magnitude of the drift, values were measured under the experimental conditions used in the work on response time, at a flow-rate of 0.9 ml/min. The following values were measured for the three modes: d.c. 1×10^{-7} A/hr, normal pulse mode 5×10^{-7} A/hr, and differential pulse mode 1×10^{-6} A/hr. For metol this corresponds to about 10^{-5}, 10^{-4} and 10^{-4} mole.l^{-1}.hr^{-1} respectively.

In the course of the drift measurements, periodical fluctuations (of several hundred nA) of the base-line were observed for the normal pulse mode. The frequency of these variations corresponds to the time between two successive pulses. This was verified by varying the pulse intervals (0.5, 1, 2 and 5 sec). Although we could not trace the origin of these interfering current pulses, we suppose that the instrument cannot deal properly with the large residual currents found in pulse voltammetry at solid electrodes and due to electrochemical reactions of the electrode material itself.[12]

The static noise of the detector was obtained in the same way as described previously.[3,13] Values are tabulated in Table 1. As only two samples are taken in the pulse modes in integrating the noise during 1 sec, these values are not taken into account.

It is clearly shown that the d.c. mode exhibits the lowest static noise. It is more difficult to draw a clear conclusion with respect to the difference in results obtained under hydrostatic flow conditions and with flows obtained by means of a peristaltic pump.

Selectivity

In the d.c. and normal pulse modes, all oxidizable compounds with half-wave potentials near or below the applied indication potential will contribute to the anodic current measured. A different situation exists in the differential pulse mode, particularly for compounds that can be reversibly oxidized at the electrode. Owing to the peak shape of the differential pulse voltammograms, the contribution of a certain compound to the resulting current will decrease, the more the indication potential differs from the peak potential of the compound. If the difference is more than $360/n$ mV, the contribution will be less than 1%.

Swartzfager[7] has published chromatograms intended to illustrate the selectivity in differential pulse detection using a carbon paste electrode, but no quantitative results were presented.

In order to test the selectivity with our detector without preceding chromatographic separation, two compounds (tyramine and isoproterenol) were taken. The half-wave potentials differ considerably, as can be seen from Fig. 4. Although it might be expected

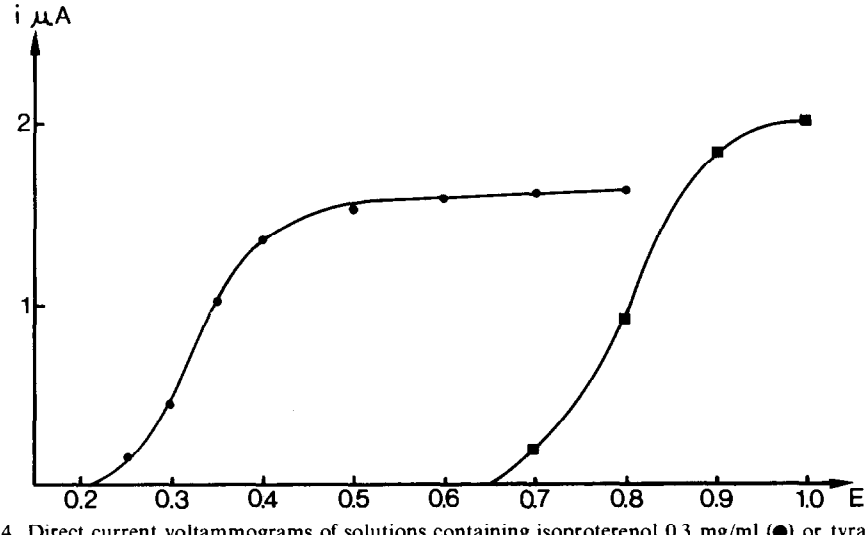

Fig. 4. Direct current voltammograms of solutions containing isoproterenol 0.3 mg/ml (●) or tyramine 0.3 mg/ml (■). Solvent: 3% propan-1-ol, 0.3% sodium dodecylsulphate, $2 \times 10^{-4}M$ Na citrate, $0.05M$ KCl adjusted to pH 2.5 with $HClO_4$.

Table 2. Peak currents for tyramine in the differential pulse mode*

i_p, μA tyramine 0.3 mg/ml	Std. devn., % (no. of detns.)	i_p, μA tyramine 0.3 mg/ml + isoprot. 0.3 mg/ml	Std. devn., % (no. of detns.)	Difference in i_p, %
13.2	5% (5)	16.2	5% (4)	+23

* Potential adjusted to 0.775 V; pulse amplitude 50 mV.

that selective detection of tyramine in the presence of isoproterenol would be possible, rather poor results were obtained (Table 2). The large relative error is probably caused by the irreversible behaviour of isoproterenol.

Adsorption

Frequently the products formed after oxidation of organic compounds are adsorbed onto the electrode. In the normal pulse mode the indication potential is applied to the electrode during a short interval. This implies that the amount of oxidized products is small in comparison to the amounts formed in the two other modes. Moreover, stripping of the adsorbed oxidation products by means of reduction or merely by desorption might be accomplished by a proper choice of the rest potential. Hence, it is generally stated that in the normal pulse mode accumulation of oxidation products is of minor importance as compared to the d.c. and differential pulse modes. In order to test this statement, a compound should be used which gives oxidation products that will be strongly adsorbed. Amitriptyline, a tricyclic antidepressant, is expected to meet this requirement. Two experiments have been carried out to compare d.c. and normal pulse detection with respect to adsorption:

(*i*) current measurements under static conditions, *i.e.*, the sample solution is passed through the cell continuously;

(*ii*) measurements of the maximum currents after repeated injections of small volumes of the sample solution.

For (*i*) the experimental arrangement used for the response time investigation was used. An amitriptyline solution (1 mg/ml) was passed through the cell at a flow-rate of 0.3 ml/min. An indication potential of 0.9 V was used for both the d.c. and the normal pulse mode. As no information could be obtained about a stripping potential, the rest potential was made as negative as possible without reduction of oxygen. A value of −0.1 V was used.

It can be seen from the current–time curve that in the d.c. mode the current reached a steady-state value after a period of about half an hour. When, subsequently, a potassium chloride solution was passed through the cell, a slow decrease of the current was observed (Fig. 5a). The only possible explanation is that during this stage adsorbed species are oxidized.

In the normal pulse mode, the current remains constant in the period of investigation apart from a small deviation during the first minute after the sample flow is started (Fig. 5b).

For (*ii*) a sample was injected every 2 mins during 2 hr. The maximum currents obtained in the d.c. mode after syringe injections of small volumes of an amitriptyline solution (1 mg/ml) are represented in Fig. 6. Here again a decrease is observed during the first stage, after which a constant value is obtained. In the normal pulse mode, the maximum currents remain constant, the relative standard deviation being 3% (52 variates).

These two experiments prove that in the normal pulse mode, under the selected conditions, either no noticeable adsorption occurs or the oxidation products formed are stripped. Similar results were obtained by Štulík and Hora[14] in testing the electrochemical cleaning of a rotating platinum electrode surface by applying periodic pulses of proper polarity; they used the Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu systems.

A qualitative explanation of the current–time curve of Fig. 5a can be given if the following aspects are taken into consideration: amitriptyline is slowly (electrochemically irreversible) oxidized at the electrode surface and consequently the concentration of amitriptyline at the surface can be taken as equal to the bulk concentration; in the oxidation at least two electrons are involved per amitriptyline molecule.[15] If it is assumed that the two electrons are transferred in two consecutive steps, the reaction can be written as:

$$R \xrightarrow[k_1;k_2]{-e} Ox_1 \xrightarrow[k_3]{-e} Ox_2$$

in which it is supposed that both the intermediate product Ox_1 and Ox_2 can be strongly adsorbed. Furthermore, it will be assumed that the rate constant for the oxidation of R at "free" sites (k_1) is larger than the rate constant at sites occupied by Ox_1 or Ox_2 (k_2); the rate constant for the consecutive oxidation of Ox_1 (k_3) is supposed to be small. The first stage of the current–time curve is then characterized by the gradually increasing coverage of the surface by Ox_1, and hence a decrease of the current. The steady state is reached when almost the whole surface is covered and the current will be determined by the oxidation of R to Ox_1 at occupied sites and the oxidation of adsorbed Ox_1 to Ox_2. In the last stage no R is supplied and the only oxidation process that can proceed is the gradual oxidation of Ox_1 to Ox_2.

To allow a simple quantitative treatment of the model suggested above, a conditional rate constant, k_{ef}, will be introduced. The value of this constant is

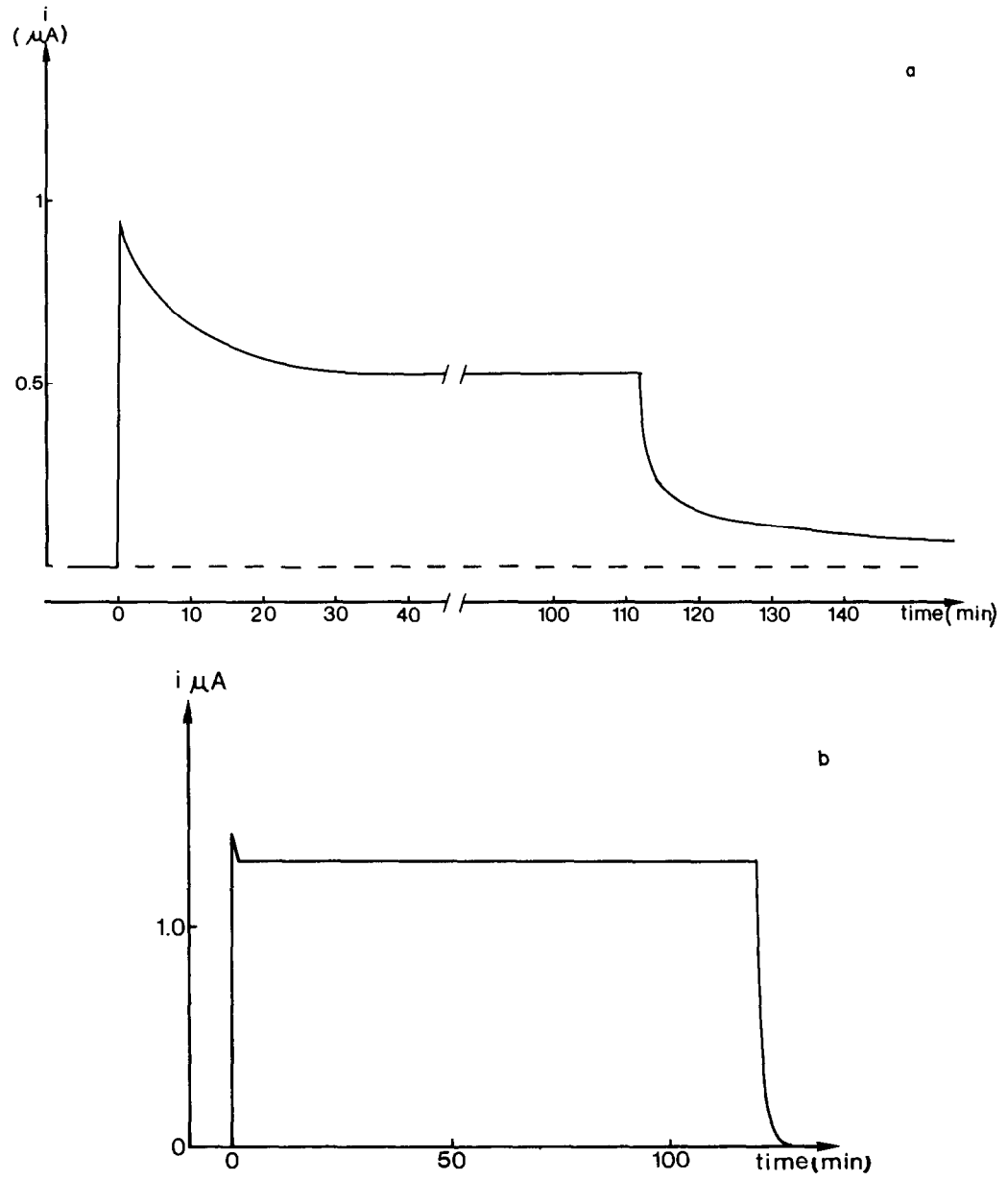

Fig. 5(a). Current–time curve (d.c. mode) of an amitriptyline solution, syphoned hydrostatically. Indication potential +0.9 V. Flow-rate 0.3 ml/min. (*b*) Current corrected for drift *vs.* time (normal pulse mode); the experimental conditions are the same as for (*a*).

supposed to be a linear combination of k_1 and k_2:[16]

$$k_{ef} = k_1(1 - \theta) + k_2\theta \quad (1)$$

where

$$\theta = \frac{\Gamma_{Ox_1}}{\Gamma_{max}} \quad (2)$$

is the degree of coverage of the electrode; Γ_{Ox_1} denotes the number of moles per unit of surface area.

The total current can be represented by:

$$i = AnF[R]k_{ef} + AnFk_3\Gamma_{Ox_1} \quad (3)$$

where A is the electrode area.

Substitution of equation (1) in equation (3) yields, after some rearrangement:

$$i = AnF[R]\{(k_1 - k_2)(1 - \theta) + k_2\} + AnFk_3\Gamma_{Ox_1}. \quad (4)$$

As the change of θ with time must be proportional to the number of free sites available at any moment:

$$\frac{d\theta}{dt} = qAnF[R]k_1(1 - \theta) \quad (5)$$

where q is a proportionality constant.

This differential equation can be solved by using the boundary conditions:

$$t = 0 \rightarrow \theta = 0$$

$$t = \infty \rightarrow \theta = 1$$

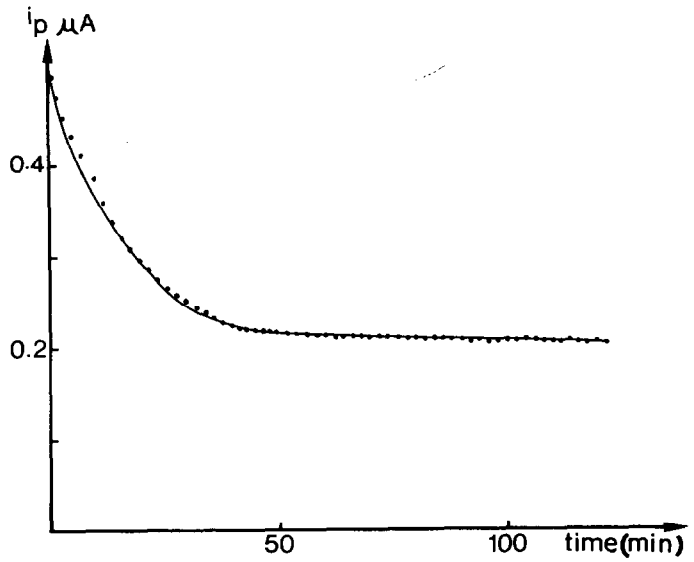

Fig. 6. Decay of the peak currents from syringe injections (d.c. mode). Indication potential +0.9 V. Flow-rate 1 ml/min.

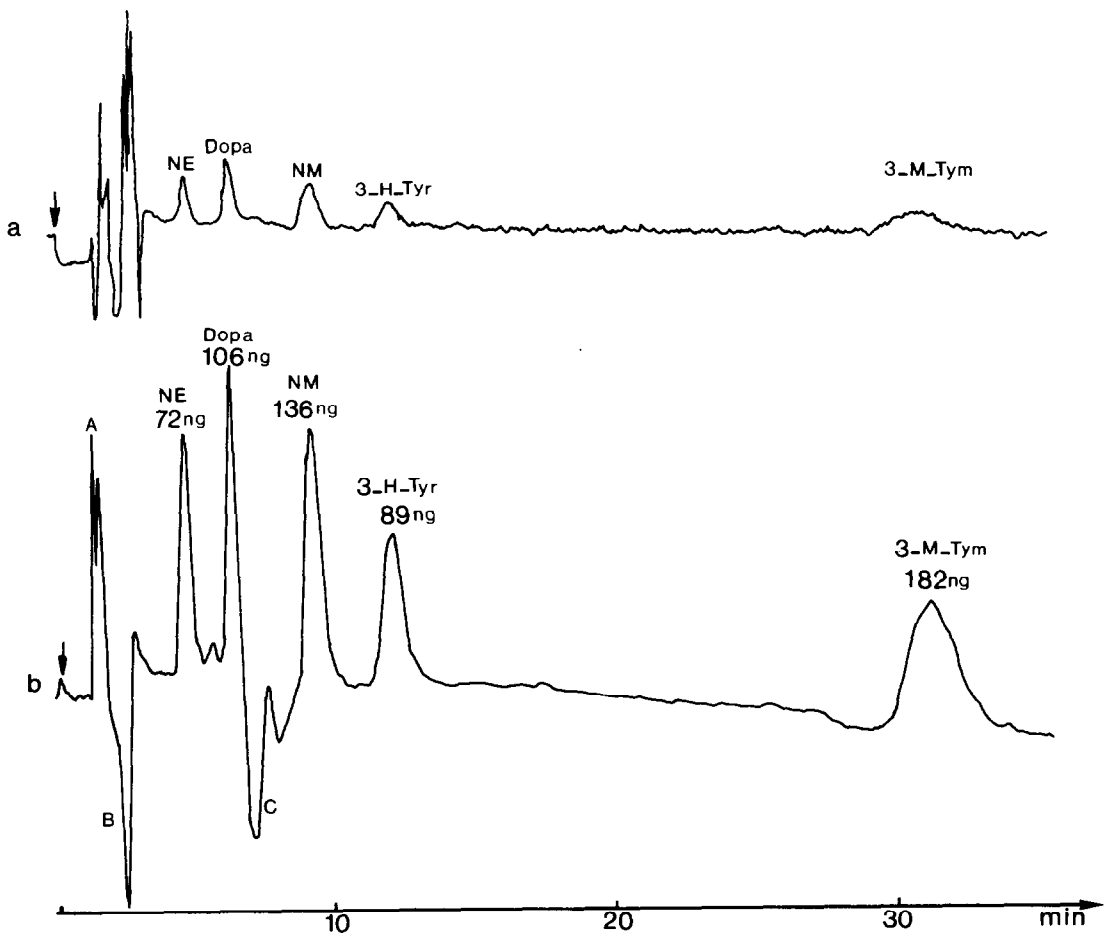

Fig. 7. Chromatograms of catecholamines and related compounds at nanogram level with the ultraviolet detector (*a*) and the electrochemical detector (*b*) in series. NE (=Norepinephrine), Dopa (=3,4-dihydroxyphenylalanine), NM (=normetanephrine), 3-H-Tyr (=dopamine), 3-M-Tym (=3-methoxytyramine).

The result is

$$\theta = 1 - \exp[-qAnF[\mathrm{R}]k_1 t]. \quad (6)$$

Substitution of equation (6) into equation (4) results in:

$$i = AnF[\mathrm{R}]\{k_2 + (k_1 - k_2)\exp[-qAnF[\mathrm{R}]k_1 t]\} + AnFk_3\Gamma_{\mathrm{Ox}_1}. \quad (7)$$

In the steady state:

$$i = AnF[\mathrm{R}]k_2 + AnFk_3\Gamma_{\mathrm{Ox}_1}. \quad (8)$$

Thus, the current change, Δi, in the first stage is represented by equation (7) minus equation (8):

$$\Delta i = AnF[\mathrm{R}](k_1 - k_2)\exp[-qAnF[\mathrm{R}]k_1 t]. \quad (9)$$

A plot of $\log \Delta i$ *vs.* t should yield a straight line. This is actually found. In the last stage of the current–time curve only the oxidation of Ox_1 has to be taken into consideration:

$$i = AnFk_3\Gamma_{\mathrm{Ox}_1}. \quad (10)$$

As

$$i = -nF\frac{\mathrm{d}\Gamma_{\mathrm{Ox}_1}}{\mathrm{d}t} \quad (11)$$

this leads to:

$$i = AnFk_3\Gamma_{\max}\,\mathrm{e}^{-Ak_3 t}. \quad (12)$$

Experimentally, the decrease of the current is not exponential when the supply of R is stopped. Obviously, the oxidation of Ox_1 proceeds in a more complicated way.

Application of the cell as a detector in HPLC

Figure 7 shows two chromatograms of catecholamines and related compounds at nanogram level, with the ultraviolet detector (*a*) and the electrochemical detector (*b*) in series. The latter detector was used in the d.c. mode with an indication potential of +0.75 V. The electrochemical detector exhibits the better signal-to-noise ratio and should be preferred. The extra positive peak A and negative peak B are artefacts caused by the solvent used for the sample. If the sample is dissolved in the eluent, both peaks disappear. The negative peak C remains; it was shown to be caused by iron introduced into the eluent by corrosion of the stainless-steel column and the leads used. The iron will be at least partly present in the bivalent state. At the indication potential used iron(II) will be oxidized to iron(III), giving rise to an offset of the base-line in the chromatogram. On injection of a sample that does not contain iron(II), the concentration level of iron(II) is decreased, leading to a lowering of the anodic base-line current and the appearance of a negative peak. The fact that the negative peak has a certain retention time is caused by the cation-exchange equilibrium in which iron(II) is involved. A proof of this explanation was found (*a*) by injection of a sample with an excess of iron(II), which led to a positive peak with the same retention time, and (*b*) by lowering the indication potential to such a value that iron(II) cannot be oxidized; in that case the peak C disappeared.

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MICRODETERMINATION OF Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Hg, Pb, Bi AND U IN INORGANIC AND ORGANOMETALLIC COMPOUNDS WITH MORPHOLINIUM MORPHOLINE-*N*-DITHIOCARBOXYLATE

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Summary—The chelates of morpholinium morpholine-*N*-dithiocarboxylate with manganese(II), iron(II), iron(III), cobalt(II), nickel, copper(II), zinc, silver, cadmium, mercury(II), lead, bismuth and uranium(VI) have been prepared and their compositions elucidated. Simple, accurate and relatively rapid procedures for the gravimetric and titrimetric microdetermination of these metals in inorganic and organometallic compounds are presented.

Morpholinium morpholine-*N*-dithiocarboxylate (MMDC) has been found to be a useful analytical reagent for the spectrophotometric determination of some 34 elements.[1] The reagent has been applied to determination of metals in biological fluids, *e.g.*, enzymes,[2] beef liver and beef pancreas,[3] also in alloys.[4]

The aim of the present work was (*i*) preparation and elucidation of the composition of metal chelates of the reagent and (*ii*) use of this reagent for gravimetric and titrimetric microdetermination of metals in inorganic and organometallic compounds.

EXPERIMENTAL

*Preparation of morpholinium morpholine-*N*-dithiocarboxylate (MMDC)*

A solution of morpholine (0.2 mole, 17.4 g) in ethanol (100 ml) is added to an ethanolic solution of carbon disulphide (0.1 mole, 7.6 g) with constant stirring. The crystalline precipitate is filtered off, washed with 95% ethanol and dried at 80°. The reagent is almost white, soluble in water and non-hygroscopic, with m.p. and mixed m.p. 105°.[2]

Preparation of chelates of MMDC

To the metal salt solution (0.005 mole in 20 ml of water), 10 ml of an aqueous solution of MMDC (0.005 mole for Ag^+; 0.01 mole for Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and UO_2^{2+}; 0.015 mole for Fe^{3+} and Bi^{3+}) are added with constant stirring.

The precipitate formed is left at room temperature for 2 hr, filtered off, washed with water (4 portions, each 2 ml) and dried for 1 hr at 150°, except for the ferric chelate which is similarly prepared but dried under vacuum for 2 hr, the manganese chelate which is left for 2 hr at 0° after precipitation, filtered off, washed with cold water (2 portions, each 2 ml) and dried under vacuum for 2 hr, and the silver chelate which is kept in the dark before filtration and during drying under vacuum. The results are given in Table 1.

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Preparation of morpholinium thiocyanate

A solution of MMDC (0.01 mole; 2.5 g in 10 ml of water) is treated with concentrated hydrochloric acid (0.02 mole; 0.73 g). To the reaction mixture a solution of potassium thiocyanate (0.02 mole; 1.94 g in 10 ml of water) is added. The mixture is evaporated to dryness, and treated with absolute ethanol, from which morpholine thiocyanate separates quantitatively as white crystals with m.p. and mixed m.p.[7] of 112.5–115° (found: C, 41.3%; H, 6.2%; N, 19.5%; S, 22.1%; $C_5H_{10}N_2OS$ requires: C, 41.0%; H, 6.8%; N, 19.1%; S, 21.9%).

Reagents

Mixed indicator. Methyl Red (50 mg) and Bromocresol Green (75 mg) in 100 ml of ethanol.

*Potassium thiocyanate solution, 0.01*M. Freshly prepared.

*MMDC solution, 0.01*M.

Analysis of inorganic compounds

A 10-mg sample is brought into solution (20 ml) and treated with exactly 10 ml of 0.01*M* MMDC with constant stirring. The solution is left at room temperature for 2 hr; for manganese the solution is kept at 0°, and for silver direct light is avoided.

Gravimetric finish. The precipitate is filtered off, washed with four 2-ml portions of distilled water, and dried at 150° to constant weight. The weighing forms are given in Table 1. The manganese, ferric and silver chelates are dried under vacuum for 2 hr at room temperature.

Titrimetric method. The filtrate and washings are heated to 60°, and 2 drops of mixed indicator are added. The excess of MMDC is titrated with 0.01*M* hydrochloric acid till a red colour just appears. A blank is carried out under the same conditions.

Alternative titrimetric method. The filtrate is treated with a slight excess of 0.01*M* hydrochloric acid and 2 drops of 5% ferric alum solution are added. The morpholinium hydrochloride formed is titrated with 0.01*M* potassium thiocyanate to the first appearance of a red colour. A blank is carried out under the same conditions.

Potentiometric titration of inorganic compounds. The water used is twice distilled. A saturated calomel and a glass electrode are used. The apparatus is standardized with a standard buffer[7] before the titration.

A 0.1-mmole sample of the inorganic compound is accurately weighed and brought into solution (100 ml). A measured excessive volume (100 ml) of 0.01*M* MMDC is added and the mixture is vigorously stirred with a mag-

Table 1. Elemental analyses of products

Complex	Colour	Found %					Theory, %					Remarks
		Metal	C	H	N	S	Metal	C	H	N	S	
$C_{10}H_{16}N_2O_2S_4Mn$	B–V	14.0	31.4	4.6	7.1	34.0	14.5	31.7	4.3	7.4	33.8	dec. at 100°
$C_{10}H_{16}N_2O_2S_4Fe$	B–V	14.5	31.3	4.2	7.1	33.9	14.7	31.6	4.2	7.4	33.7	stable up to 500°
$C_{15}H_{24}N_3O_3S_6Fe$	B–V	10.3	33.6	4.4	7.6	35.6	10.3	33.2	4.5	7.7	35.5	m.p. 140°, loses consistency at 12°
$C_{10}H_{16}N_2O_2S_4Co$	G	15.4	31.2	4.2	7.3	33.4	15.4	31.3	4.2	7.3	33.4	stable up to 500°
$C_{10}H_{16}N_2O_2S_4Ni$	Y–G	15.0	31.6	4.3	7.4	33.7	15.3	31.4	4.2	7.3	33.5	stable up to 285°
$C_{10}H_{16}N_2O_2S_4Cu$	B	16.2	30.7	4.2	7.5	32.9	16.4	31.0	4.2	7.2	33.1	stable up to 282°
$C_{10}H_{16}N_2O_2S_4Zn$	W	16.6	30.6	4.2	7.1	32.6	16.8	30.8	4.1	7.2	32.9	stable up to 500°
$C_5H_8NOS_2Ag$	W	39.8	22.0	3.1	5.0	23.6	39.9	22.2	3.0	5.2	23.7	blue-white in daylight; dec. on heating
$C_{10}H_{16}N_2O_2S_4Cd$	W	25.6	27.3	3.9	7.2	29.0	25.8	27.5	3.7	7.3	29.3	stable up to 500°
$C_{10}H_{16}N_2O_2S_4Hg$	W	38.5	22.6	3.0	5.1	24.7	38.2	22.9	3.1	5.4	24.4	stable up to 500°
$C_{10}H_{16}N_2O_2S_4Pb$	Y–W	38.5	22.7	3.1	5.4	24.5	38.8	22.6	3.0	5.3	24.1	stable up to 290°
$C_{15}N_{24}N_3O_3S_6Bi$	Y	29.8	26.5	3.4	6.1	27.0	30.0	25.9	3.5	6.0	27.6	stable up to 280°
$C_{10}H_{16}N_2O_4S_4U$	O	39.7	19.8	2.8	4.5	21.0	40.0	20.2	2.7	4.7	21.5	stable up to 220°

B = brown; V = violet; G = green; Y = yellow; W = white; O = orange.

Table 2. Analysis of compounds (range of 3–6 results)

Compound	Theoretical	Metal content, %* Gravimetric	Potentiometric	HCl titration	KSCN titration
$FeSO_4.7H_2O$	20.09	19.8–20.2	19.8–20.3	20.1–20.2	20.0–20.2
$FeCl_3.6H_2O$	20.66	20.5–20.8	20.4–20.5	20.6–20.7	20.5–20.7
$CoCl_2.6H_2O$	24.78	24.6	—	—	24.6–24.8
$Co(NO_3)_2.6H_2O$	20.26	20.2–20.3	20.2–20.5	24.5–24.6	—
$NiCl_2.6H_2O$	24.69	24.6–2.49	—	—	24.5–24.8
$NiSO_4.7H_2O$	20.91	20.8–20.9	20.7–20.9	24.5–2.48	—
$CuSO_4.5H_2O$	25.45	25.3–25.4	25.2–25.7	25.2–25.7	25.3–25.6
$ZnSO_4.7H_2O$	22.74	22.5–23.0	23.0	22.7–23.0	22.7–22.9
$AgNO_3$	63.5	63.3–63.7	63.2–63.8	63.3–63.7	63.3–63.7
$Cd(NO_3)_2$	47.55	47.4–47.5	47.3–47.6	—	—
$HgCl_2$	73.85	73.6–73.9	73.7–74.1	73.6–73.8	73.7–74.1
$Pb(NO_3)_2$	62.56	62.4–62.7	62.5–62.6	62.5–62.8	62.4–62.8
$UO_2(NO_3)_2.6H_2O$	47.40	47.2–47.4	47.1–47.6	47.2–47.6	47.2–47.6
$MnSO_4.H_2O$	32.54	32.3–32.4	—	32.6–32.8	32.4–32.5
$CdBr_2$	41.29	41.1–41.5	—	41.1–41.3	41.2–41.3
$Bi(NO_3)_3.5H_2O$	43.08	42.9–43.3	—	43.0–43.3	43.1–43.3
$Mn(CH_3COO)_2.4H_2O$	22.42	22.2–22.3	—	22.3	22.3–22.5
$FeC_2O_4.2H_2O$	31.06	30.9	30.8–20.9	30.9–31.1	31.1–31.2
$Fe(C_9H_6NO)_3$	11.44	11.2–11.3	11.4–11.6	11.3	11.3–11.5
$Co(CH_3COO)_2$	33.29	33.1–33.2	—	33.1–33.2	33.2–33.5
$Ni(C_4H_7O_2N_2)_2$	20.31	20.2–20.4	—	20.1–20.4	20.3–20.4
$Cu(CH_3COO)_2.H_2O$	31.85	31.6–31.8	—	31.7	31.8–31.9
$Cu(C_6H_5COO)_2$	20.79	20.8–21.0	—	20.9–21.0	—
$Zn(C_5H_5N)_2(SCN)_2$	19.24	19.2–19.4	—	19.3–19.4	—
$Zn(CH_3COO)_2.H_2O$	29.80	29.7–29.9	29.6–30.1	—	29.5–29.8
$Ag_2C_2O_4$	71.03	70.8–71.1	70.8–71.3	71.0–71.3	71.2–71.3
$Cd(C_9H_6NO)_2$	28.05	28.0–28.2	—	28.0–28.2	28.1
HgC_2O_4	69.51	69.4–69.7	69.6–69.8	69.3–69.7	69.3–69.7
$Pb(CH_3COO)_2.3H_2O$	54.63	54.4–54.9	—	54.6–54.9	54.6–54.8
$Bi_2(C_2O_4)_3.7H_2O$	51.73	51.5–51.7	—	51.8–52.0	51.6–51.9
$BU_2(CH_3COO)_2.2H_2O$	56.13	56.0	56.0–56.4	55.9–56.7	56.0–56.4

netic stirrer. The solution is heated to 60° and the excess of MMDC is titrated potentiometrically with 0.2*M* hydrochloric acid. A blank is done under the same conditions.

Analysis of organometallic compounds

A 10-mg sample is treated with a mixture of 0.5 ml of concentrated hydrochloric acid and 0.3 ml of concentrated nitric acid. For silver compounds nitric acid alone is used for the digestion. The mixture is heated gently at 70° till nearly dry, then 0.8 g of urea is added to ensure complete removal of nitrogen oxides and nitrous acid, followed by 10 ml of distilled water. The solution is then neutralized to Methyl Orange with 8*M* ammonia solution. The solution is heated for 10 min, then the analysis is completed as for inorganic compounds.

RESULTS AND DISCUSSION

The conversion factors for the gravimetric determinations are: 0.1448 for manganese, 0.1470 for iron(II), 0.1029 for iron(III), 0.1539 for cobalt, 0.1532 for nickel, 0.1637 for copper, 0.1679 for zinc, 0.3994 for silver, 0.2576 for cadmium, 0.3824 for mercury(II), 0.3897 for lead, 0.3004 for bismuth and 0.4004 for uranium.

In the back-titration method with hydrochloric acid, the decomposition rate of MMDC is increased at 60° and one mole of the reagent reacts with 2 moles of the acid.[5]

In this titration, 1 ml of 0.01*M* MMDC is equivalent to 0.2747 mg of Mn, 0.2793 mg of Fe^{2+}, 0.1862 mg of Fe^{3+}, 0.2947 mg of Co, 0.2935 mg of Ni, 0.3177 mg of Cu, 0.3269 mg of Zn, 1.079 mg of Ag, 0.5621 mg of Cd, 1.003 mg of Hg, 1.036 mg of Pb, 0.6967 mg of Bi and 1.190 mg of U.

In acidic medium, MMDC undergoes decomposition into carbon disulphide and morpholine hydrochloride.[5,6] On titration with potassium thiocyanate, ion-exchange takes place, giving morpholinium thiocyanate. The conversion factors for this method will be the same as for the other back-titration method.

With organometallic compounds the most important problem is the decomposition: *aqua regia* is generally suitable. For organic uranium compounds a mixture of hydrochloric acid and hydrogen peroxide can be used. Organic silver compounds are digested in concentrated nitric acid alone to avoid precipitation of silver chloride. With organic ferrous compounds the nitric acid in the *aqua regia* has a dual function; it acts as an efficient solvent and also oxidizes the ferrous ion to the ferric state. Complete removal of nitrogen oxides and nitrous acid is ensured by addition of urea. The results are summarized in Table 2, and are generally within the accepted limits of error.

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DETERMINATION OF SUBMICROGRAM AMOUNTS OF VANADIUM IN BIOLOGICAL MATERIALS BY EXTRACTION WITH *N*-CINNAMOYL-*N*-2,3-XYLYLHYDROXYLAMINE AND FLAMELESS ATOMIC-ABSORPTION SPECTROMETRY WITH AN ATOMIZER COATED WITH PYROLYTIC GRAPHITE

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Summary—A highly sensitive and simple method for determination of vanadium in plants and biological samples by solvent extraction and flameless atomic-absorption spectrometry with a carbon tube coated with pyrolytic graphite is described. After digestion of the sample, vanadium is separated by extraction of its *N*-cinnamoyl-*N*-2,3-xylylhydroxylamine complex into carbon tetrachloride from 6*M* hydrochloric acid medium. The method can be used to determine vanadium in plants and biological samples with average recovery of 94% and coefficient of variation of 14%. The sensitivity (1% absorption) is estimated to be 4×10^{-11} g.

The most widely used method for determination of trace amounts of vanadium in biological materials is neutron-activation analysis.[1,2] The major difficulties with this method are that the procedure is complicated by the short half-life of ^{52}V (3.75 min) and that the ^{52}V activity is masked by the ^{24}Na which is produced in relatively large amounts from the matrix. Recently a flameless atomic-absorption spectrometry (AAS) method using a carbon-tube atomizer for the determination of trace elements in biological materials has been reported.[3–6] The use of such a method for determination of vanadium in biological materials is impossible because the vanadium absorbance is depressed by accompanying elements[7] (*e.g.*, Ca, Fe and Mo), and decreased by the soaking of vanadium into the carbon tube and the formation of undissociated vanadium carbide in the ashing or atomizing stage by reaction of vanadium with the carbon tube. For the determination of trace amounts of vanadium it is necessary to find a reagent which reacts with vanadium selectively to form a compound which does not soak into the carbon tube and that gives a sufficiently high absorbance. Shome[8] has reported *N*-benzoyl-*N*-phenylhydroxylamine (BPA) as a chelating reagent for vanadium. However, BPA cannot be applied in the flameless AAS method for trace levels because it cannot extract vanadium at the ng level. *N*-Benzoyl-*o*-tolylhydroxylamine (BTA) has been recommended by Majumdar and Das,[9] but this also is not suitable for flameless AAS analysis for trace amounts of vanadium, because a portion of the vanadium complex is soaked into the carbon tube and the necessary sensitivity cannot be obtained. Priyadarshini and Tandon[10] have reported on *N*-cinnamoyl-*N*-phenylhydroxylamine (CPA) as chelating reagent. In flameless AAS analysis, the sensitivity with this complex is better than that with the BTA complex of vanadium, but other elements in the matrix are extracted simultaneously with vanadium. The following conclusions may be drawn from their studies. (1) Compounds derived from BPA by introduction of one or two methyl groups into the *N*-phenyl groups will react with trace amounts of vanadium selectively. (2) The complexes of the cinnamoyl analogues of BPA will be less liable to soak into the carbon tube, possibly because the cinnamoyl groups are bulkier than benzoyl groups. On this basis, we synthesized a new reagent, *N*-cinnamoyl-*N*-2,3-xylylhydroxylamine (CXA), which was found to behave as predicted, giving selective extraction of trace amounts of vanadium and enhancing the vanadium absorbance by a factor of about $3\frac{1}{2}$ (compared with that of the BTA complex). A carbon tube coated with pyrolytic graphite was used, to avoid the formation of undissociated vanadium carbide,[11] and this gave a further enhancement of the sensitivity. The proposed method gives about 12 times the sensitivity of our previous method[12] (BTA as chelating reagent; conventional carbon tube).

EXPERIMENTAL

Reagents

All solutions were prepared from distilled water and analytical grade reagents.

Standard vanadium(V) solution, 1000 ppm. Prepared immediately before use, by dissolving 0.148 g of ammonium metavanadate in a minimum quantity of ammonia solution and diluting to 500 ml with water.

Standard vanadium(IV) solution, 1000 ppm. Prepared immediately before use by dissolving 1.953 g of vanadyl sulphate in 0.9*N* sulphuric acid and diluting to 500 ml with water.

Potassium permanganate solution, 0.02M.

CXA solution, 0.1%, in carbon tetrachloride. The CXA was synthesized by the method used for BTA by Majumdar and Das.[9] In a 1-litre beaker were placed 2 g of ammonium chloride, 20 ml of water, 30 ml of ethanol and 35 g of 2,3-dimethylnitrobenzene. The mixture was stirred vigorously with a mechanical stirrer, and 50 g of zinc dust were slowly added. Stirring was continued for 30 min after all the zinc dust has been added. While still hot, the solution was filtered by suction to remove the zinc oxide, which was washed with 20 ml of ether and finally with water. The filtrate was made slightly alkaline with sodium hydrogen carbonate. Cinnamoyl chloride (*ca.* 15 g) was then added dropwise, while the 2,3-dimethylhydroxylamine solution was stirred vigorously and kept alkaline with sodium hydrogen carbonate. The stirring was continued for about 30 min. The resulting solid was filtered off and washed with water. The product was extracted with ammonia solution and the ammoniacal solution was added slowly to ice-cold dilute sulphuric acid. The *N*-cinnamoyl-*N*-2,3-xylylhydroxylamine that separated out was filtered off and further purified by recrystallization from aqueous ethanol. The white crystals had m.p. 132°. Found—C, 76.4%; H, 6.3%; N, 5.3%; calculated—C, 76.40%; H, 6.37%; N, 5.24%.

Apparatus

A Hitachi Model 170-50 atomic-absorption spectrometer, equipped with a Hitachi Model GA-2 heated-graphite atomizer and a deuterium background-corrector, was used. A Hitachi Model 056 recorder (10-mV range) was used to record peak-heights. A Jintan 50-μl microsyringe was used for injecting test solutions into the carbon tube.

Instrument settings. The 318.4 nm vanadium resonance line was used. The line-source was a Hitachi vanadium hollow-cathode lamp operated at 10 mA. Background correction was used for all measurements. Control settings on the GA-2 were experimentally optimized and provided the following drying, ashing and atomizing conditions: dry by raising the current from 0 to 25 A at 1 A/sec (final temperature *ca.* 100°), ash at 150 A (*ca.* 1850°) for 20 sec, atomize at 300 A (*ca.* 2800°) for 10 sec. Argon was used as the furnace purge-gas at a flow-rate of 2.6 l./min.

Procedure

The sample (viscera and flesh 1–10 g; blood 10 ml; urine 50 ml) was digested with nitric acid and perchloric acid. The digested solution was diluted to *ca.* 30 ml with water, and transferred to a separatory funnel. To keep the vanadium in the quinquevalent state, 0.02*M* potassium permanganate was added drop by drop until a pink colour persisted for 5 min, and then 1 ml of 0.1% CXA solution in carbon tetrachloride was added, followed by *ca.* 30 ml of concentrated hydrochloric acid (to give a concentration of *ca.* 6*M* in the resulting solution). The funnel was immediately shaken for 3 min and the vanadium extracted into the carbon tetrachloride phase. Aliquots of the extract (20 μl) were injected into the carbon tube with a microsyringe, and the vanadium was determined.

RESULTS AND DISCUSSION

Effect of acidity on the extraction of vanadium(V)

For maximum extraction of vanadium the concentration of acid in the aqueous phase should be between 4 and 9*N* (see Fig. 1); most of our measurements were made at an acidity of about 6*N*. Only hydrochloric acid was suitable for adjusting the acidity, but the presence of the acids used for the digestion (nitric and perchloric) could be tolerated, provided that their concentration in the aqueous phase was less than 3*M*.

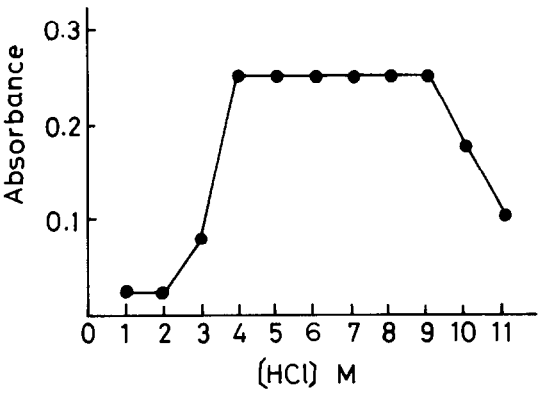

Fig. 1. Effect of acidity on the extraction of vanadium with 0.1% CXA solution in carbon tetrachloride (V, 1 ng).

Stability of vanadium(V) in 6M hydrochloric acid medium

Figure 2 shows the relationship between the vanadium absorbance and the lapse of time between addition of hydrochloric acid and extraction of vanadium. There was no change in vanadium absorbance for standing times up to 2 min, but with longer times there was partial reduction to vanadium(IV) which does not react with CXA. It is therefore desirable to extract the vanadium immediately after addition of the hydrochloric acid, and necessary to do so within 2 min of the addition.

Interferences

It was found that as little as 50 ng of vanadium could be determined in presence of a large excess of foreign ions. Al^{3+} (100 μg), As(V) (10 μg), Ba^{2+} (10 μg), Ca^{2+} (40 mg), Cd^{2+} (10 μg), Co^{2+} (10 μg), Cr(VI) (10 μg), Cu^{2+} (100 μg), Hg^{2+} (10 μg), Mg^{2+} (40 mg),

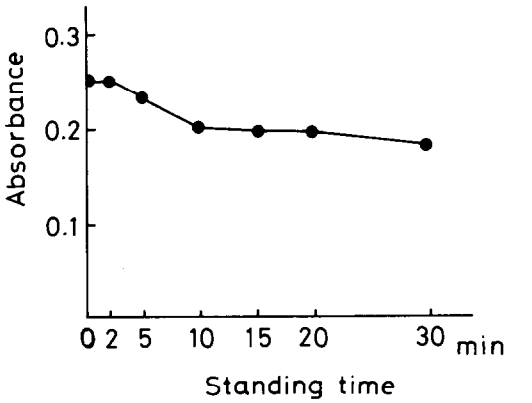

Fig. 2. Relationship between the absorbance of vanadium and the standing time of aqueous phase until the extraction of vanadium after addition of hydrochloric acid (V, 1 ng).

Table 1. Enhancement of vanadium absorbance by using the tube coated with pyrolytic graphite (V, 1 ng)

Reagent	Absorbance Carbon tube	Pyrolytic graphite coated tube
BPA	N.D.	N.D.
BTA	0.02	0.17
CXA	0.07	0.24

N.D.: not detected.

Mo(VI) (10 μg), Ni^{2+} (100 μg), Pb^{2+} (10 μg), Sb(V) (10 μg), Se(IV) (10 μg), Ti^{4+} (10 μg), Zn^{2+} (40 mg) and phosphate (20 mg) do not interfere when present at the levels shown in brackets.

Stability of vanadium–CXA complex

The extract gives the same absorbance for at least 3 days whether it is separated from the aqueous phase immediately after the extraction or left in contact with it.

Enhancement by use of a pyrolytic graphite coating on the tube

When a tube coated with pyrolytic graphite was used instead of a conventional carbon tube, the vanadium absorbance was enhanced by a factor of about $3\frac{1}{2}$ (Table 1). This seems to be due to the lower porosity of the coating, resulting in less soaking of vanadium into the carbon tube and lower formation of vanadium carbide. The increase in sensitivity relative to that for the BTA complex (by a factor of about $1\frac{1}{2}$) is attributed to soaking into the carbon tube being less for the CXA complex because CXA is bulkier than BTA.

Calibration curve and precision

Calibration curves made under the optimum conditions established were identical whether based on the vanadium(V) solution as standard or vanadium(IV) solution that had been oxidized by the digestion procedure. The linearity was good over the range 10–80 ng/ml. The sensitivity for 1% absorption was found to be 2 ng/ml. The relative standard deviation was *ca.* 3% for 50 ng/ml of vanadium(V) (10 determinations, 3 injections for each).

Applications

Table 2 shows results obtained for various types of sample. The recovery was 91–107% for samples spiked with vanadium(V) and the relative standard deviation was 2–14%. By the proposed method, 0.1 ng/g levels of vanadium in samples can be determined.

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Table 2. Results for samples analysed by proposed method

Sample	V added, *ng*	Found *ng*					Mean, *ng*	C.V. %	Recovery %
Apple (5 g)	0	34.7	38.2	38.9	36.8	38.2	37.4	4.5	
	30	66.7	69.4	69.4	69.4	64.6	67.9	3.2	101.7
Parsley (1 g)	0	115	100	100	120	120	111	9.2	
	100	200	215	210	195	200	204	4.0	93.0
Potato (1 g)	0	21.3	24.0	22.7	29.3	28.0	25.1	13.7	
	20	42.7	45.3	42.7	45.3	46.7	44.5	4.0	97.0
Undaria pinnatifida (1 g)	0	39.7	41.3	41.3	38.1	41.3	40.3	3.6	
	50	84.2	86.8	91.1	86.8	89.5	87.7	3.1	94.8
Jack mackerel (2 g)	0	31.8	30.9	30.9	29.6	27.3	30.1	5.8	
	100	123	127	132	136	136	131	4.4	100.9
Pacific saury (1 g)	0	24.6	22.1	29.5	29.5	24.6	26.1	12.7	
	100	113	123	121	125	128	122	4.6	95.9
Sardine (2 g)	0	253	259	247	247	224	246	5.4	
	100	335	335	347	335	335	337	1.6	91.0
Pig liver (10 g)	0	62	62	58	60	56	60	4.4	
	50	113	98	106	109	111	107	5.5	94.8
Pig kidney (10 g)	0	48	46	48	47	52	48	4.7	
	50	107	96	86	96	100	97	7.9	97.8
Human blood (10 ml)	0	4.6	4.6	5.0	4.8	4.5	4.7	4.3	
	10	15.0	13.0	16.0	16.6	16.4	15.4	9.6	107.0
Human urine (50 ml)	0	12.5	14.3	12.5	14.3	10.7	12.9	11.7	
	10	21.3	22.7	21.3	25.3	24.0	22.9	7.6	100.0
				μg					
Human hair (5 g)	0	0.821	0.744	0.718	0.744	0.821	0.770	6.3	
	0.500	1.36	1.23	1.26	1.18	1.23	1.25	5.4	96.0

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COULOMETRIC INVESTIGATION OF THE CONDITIONS FOR DRYING BAUXITES FOR CHEMICAL ANALYSIS

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Summary—In order to dry a bauxite sample to constant weight for the determination of alumina content, the following procedure is recommended. The sample should be placed in a small flat weighing bottle and heated at 105–110° for 5 hr in a dried atmosphere, then cooled in a desiccator containing magnesium perchlorate. After weighing, it should be reheated at 105–110° for 40–60 min then cooled and weighed under the same conditions to ensure it has attained constant weight.

Because bauxite is bought and sold commercially in large tonnages, the precise determination of its alumina content is a very important problem. The alumina content in bauxite is usually reported on a "dry" basis. Therefore, if the sample weighed has a 0.1% variation (absolute) in its water content, the alumina content for a sample containing 60% alumina may be in error by 0.06%. If we wish to determine the alumina content in a bauxite more precisely, the reproducibility of drying the sample is a major problem. Although the difficulty of drying such zeolitic materials is emphasised in the literature,[1–9] a bauxite sample for alumina analysis is usually dried simply by heating it at 105–110° for 1,[10] 2,[11] 3,[12] hr or longer. In many procedures the heating time is not shown at all, and sometimes 140° is recommended[13] to shorten it. These discrepancies indicate the difficulty in drying a bauxite sample.

Recently, we investigated the drying conditions for iron ores,[14] and indicated that the residual differences in water content of the ores are negligible if the samples are heated at 110° for 3–4 hr in a very dry atmosphere.

The drying procedure for bauxite samples has now been investigated by the same method as for iron ores. The results indicate that nearly constant weight of the sample is obtainable when the sample is heated in a dry atmosphere for somewhat longer than iron ores.

EXPERIMENTAL

The apparatus, reagents and procedure used were the same as those in the previous papers.[14,15]

The sample (0.1 g) was first heated at 110° for various time intervals in thoroughly dried argon, and cooled for 60 min in an atmosphere of argon that had been passed through a U-tube containing magnesium perchlorate. Then the sample was reheated at the same temperature as before and the water extracted by this second heating was determined by coulometry.[15,16]

Three samples were used: a commercial bauxite (Bauxite A) from the Comalco mine (Australia) and two standard samples, No. 691 (Bintan mine, Indonesia) and No. 692 (Comalco mine), which were prepared by the Light Metal Smelters' Association of Japan.

RESULTS AND DISCUSSION

Bauxite A was first used as sample. It was pulverized to pass a 200-mesh sieve. The amounts of water extracted in each 5-min period during the second heating are shown in Fig. 1. The curves in the figure are nearly the same as those for iron ores,[14] and similar conclusions can be drawn. (1) The cooled sample takes more than 15 min to reach the temperature of the furnace after its introduction into the hot zone of the furnace. (2) Strictly speaking, the sample does not reach constant weight even on heating for more than 10 hr in a very dry atmosphere; moreover, the amount of water extracted is several times that from the most hydrated iron ores. Also, water was continuously evolved at the rate of about 4 ppm/min even after several hours of heating, indicating that the sample was releasing combined water. (3) The rate of evolution was almost constant after the first 3 hr of heating, and more completely so after 5 hr. This indicates that the adsorbed water in the sample may be removed by heating for 5 hr in a dry atmosphere.

The cumulative amounts of water extracted, calculated from the curves in Fig. 1, are shown in Fig. 2. The difference in the amounts of water extracted between 5 and 10 hr of heating was very small, and indicated that the sample reached nearly constant condition after being heated for 5 hr at 110°. Prolonged heating may be harmful, however, owing to the extraction of combined water. Usually we dry a sample by heating it for several hours at 105–110° then cool and weigh. The sample is then heated again for 1 hr (or less) to make sure it has reached constant weight. The amounts of water extracted in the second

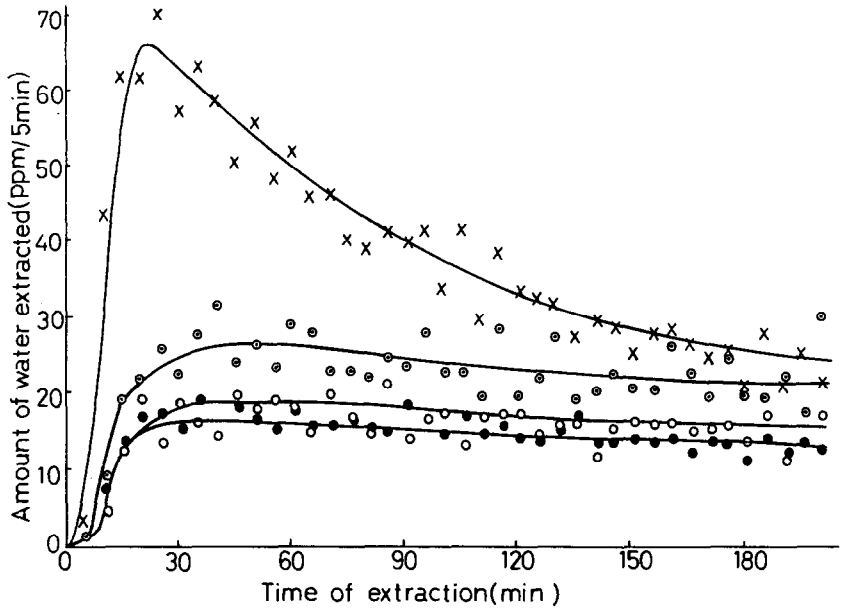

Fig. 1. The amounts of water extracted for each 5-min period during the second heating. Sample: Bauxite A; heating temperature: 110°; duration of the first heating: ×—× 1 hr; ⊙—⊙ 3 hr; ○—○ 5 hr; ●—● 10 hr.

hour of heating were deduced from the curves in Fig. 2 and plotted against the duration of first heating; the results are shown in Fig. 3. The curves in this figure indicate that the sample reaches a nearly constant state of dryness when it has been heated for 4–5 hr or more at 110° in a very dry atmosphere. Heating at 105° was also investigated and the results are shown in the same figure. The amounts of water extracted from the sample by the second heating were nearly the same as those for heating at 110°. Therefore, small differences in the heating temperature do not cause serious errors.

Figure 4 shows that the other bauxites behave in much the same way as the Comalco ore, and indicates that these samples should also be dried at 110° for 4–5 hr or more and the first heating time should be controlled more exactly for the No. 692 sample, in order to obtain constancy of drying. To shorten the heating time of the sample, heating at 140° was recommended in U.S.A.[13] However, the broken line

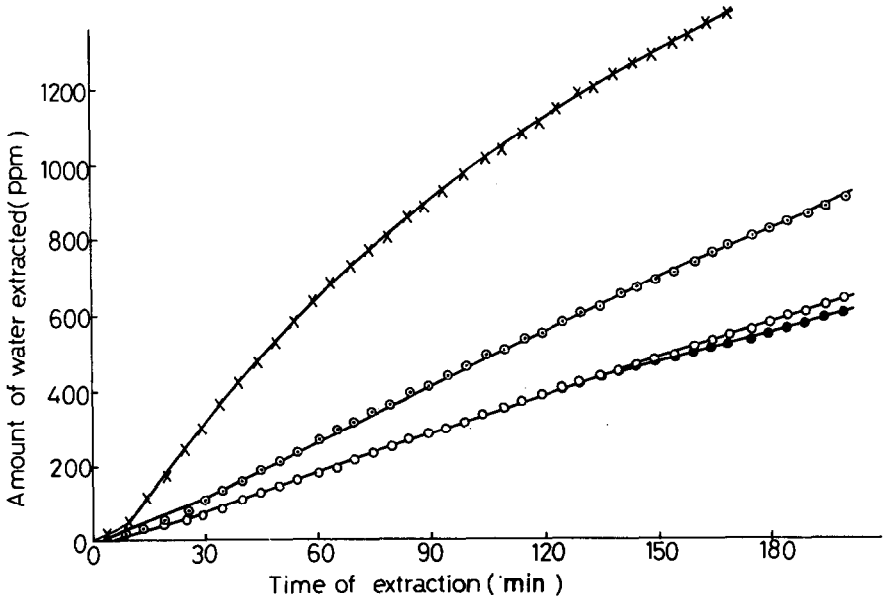

Fig. 2. The total amounts of water extracted by the second heating (calculated from the curves of Fig. 1.) The symbols mean the same as in Fig. 1.

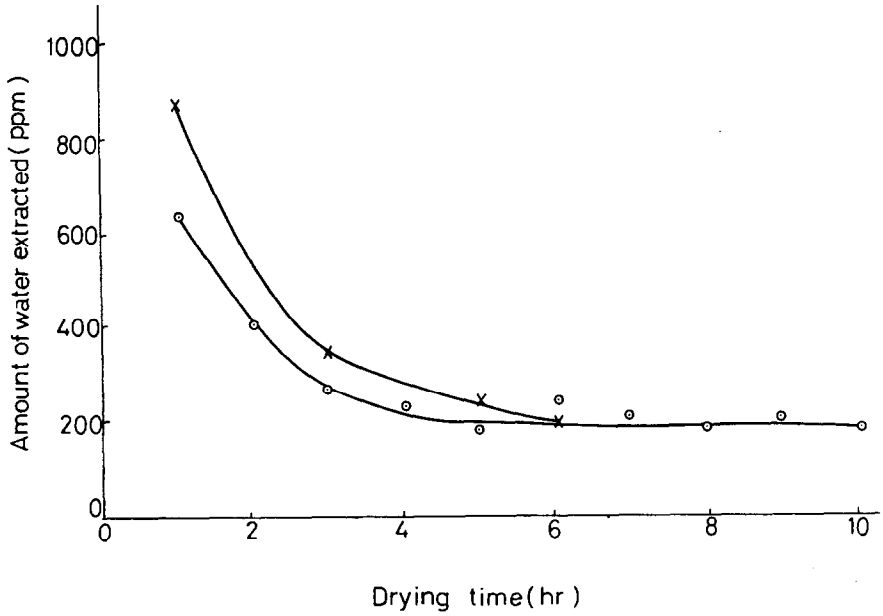

Fig. 3. The amounts of water extracted by the second hour of heating *vs.* the duration of the first heating. Sample: Bauxite A; heating temperature: ×—× 105°, ⊙—⊙ 110°.

in the figure shows that heating at higher temperature only increases the amount of water extracted. The shape of the broken line is similar to that of the full line for the same sample. This indicates that the high-temperature heating only increases the amount of extracted water and does not shorten the heating time necessary. Thus, there is no advantage in high-temperature heating.

In any case, the bauxites reach a nearly constant state of dryness when they are heated at 105–110° for 4–5 hr in a very dry atmosphere. The maximum difference between the amounts of water extracted in the second heating from the samples which were initially heated for 4 and for 5 hr was only about 0.01%, and did not cause a significant error in weighing the sample. The second heating should not be longer than 1 hr though, otherwise much combined water will be extracted.

It should be emphasised that these results were obtained by heating the samples in a very dry atmos-

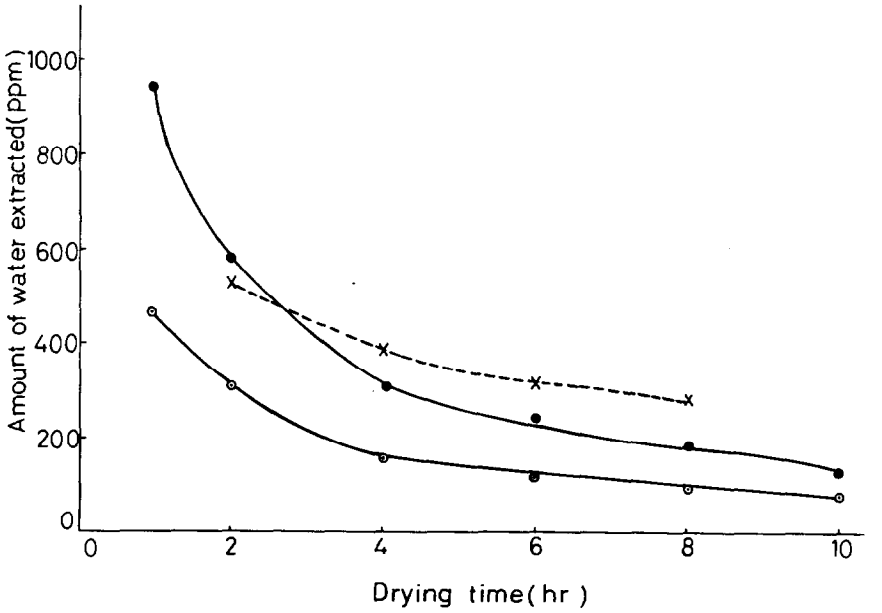

Fig. 4. The amounts of water extracted by the second hour of heating *vs.* the duration of the first heating. Sample No. 691, heating temperature: ⊙—⊙ 110°, ×—× 140°. Sample No. 692, heating temperature: ●—● 110°.

phere. If the samples are heated in an ordinary convection oven, the heating should be 3–4 times as long.[7] For the determination of only adsorbed water in bauxites the following method is recommended: the adsorbed water should be extracted into dry carrier gas by heating at 105–110° and then determined by the direct gravimetric method.[17] The heating time should not be too long, or some combined water may be evolved from the sample. Heating for 4–5 hr is enough for bauxite samples under these conditions.

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DETERMINATION OF CHLORAMPHENICOL IN PHARMACEUTICAL PREPARATIONS BY THE CADMIUM ION-SELECTIVE ELECTRODE, SPECTROPHOTOMETRY AND ATOMIC-ABSORPTION SPECTROMETRY

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Summary—New simple methods are described for the determination of chloramphenicol and its esters in pure powders, suppositories, injections, eye-drops, capsules and oral suspensions. These are based on reduction with cadmium metal whereby 6 equivalents of cadmium ions per mole and the corresponding amino-derivative are released. Four portions of the reduction products are used for (*i*) measurement of the cadmium ions by atomic-absorption spectrometry at 228.8 nm; (*ii*) potentiometric titration with EDTA, with use of the cadmium ion-selective electrode; (*iii*) visual titration with EDTA, with Eriochrome Black T as indicator; (*iv*) diazotization and coupling with *N*-(1-naphthyl)ethylenediamine and measuring the resultant colour at 550 nm. The results obtained by these procedures are in good agreement, and compare favourably with those of the official methods.

Determination of chloramphenicol and its esters has been, and is still, the subject of detailed investigations, as these broad-spectrum antibiotics are of wide therapeutic application throughout the world. Analytical procedures based on direct and indirect spectrophotometry, titrimetry, electrometry, and chromatography have been advocated.[1–3] Most of these approaches are based on the unique structure of chloramphenicol, since the nitro-group is a rather unusual structural feature in biological and biochemical systems. However, methods have also been reported involving reactions of the amide-group or the decomposition products of these compounds.

The most widely used spectrophotometric methods are based on the reduction of the nitro-group with acidic titanium(III), tin(II), zinc and aluminium[1] or alkaline sodium hydrosulphite,[4] followed by diazotization and coupling. The colour displayed by the nitro-group of chloramphenicol, in basic media, can also be measured.[5–7] Reaction with heteropoly acids,[8] isoniazide[9] and hydroxylamine[10] forms the basis of other spectrophotometric procedures. Such methods, however, are not directly applicable to the analysis of pharmaceutical preparations as most of the flavouring agents, diluents and excipients are carbonyl-containing compounds which therefore interfere.

Indirect acidimetric,[11,12] argentimetric,[13] and redox[14,15] titrations have been utilized for the determination of the hydrolysis or decomposition products of chloramphenicol. Reduction of the nitro-group into the amino-, followed by bromometric titration[16] or titration with nitrous acid[17] has also been described. However, these reactions are not always stoichiometric, and interference from many pharmaceutical excipients is frequent, necessitating a time-consuming extraction or separation step prior to analysis. Electroanalytical techniques may also be used.[3] Among these, the polarographic approach is the most important since many of the pharmaceutical additives do not interfere and the nitro-group in chloramphenicol and its esters can be differentially reduced by variation of the pH, permitting simultaneous analysis of mixtures for various components.[18] Gas chromatography,[19] high-performance liquid chromatography[20] and X-ray diffraction[21] methods have also been described.

However, the need for further investigation is evidenced by the fact that most of the reported methods for the determination of chloramphenicol and its esters are beset with difficulties during their application. These difficulties may be attributed to the unfavourable solubility of some derivatives, non-specificity and unfavourable stoichiometry of the reactions used, critical reaction conditions and interference by pharmaceutical excipients. The present investigation describes a combination of an easy reduction procedure for chloramphenicol and its esters in various pharmaceutical preparations, without prior extraction, by use of cadmium metal, followed by rapid instrumental measurement of the released cadmium ions and amine by atomic-absorption spectrometry, spectrophotometry and potentiometry.

EXPERIMENTAL

Apparatus

Digital mV/pH-meter. An Orion 901 microprocessor with cadmium ion-selective electrode (Orion 49-48) in conjunc-

tion with a double-junction reference electrode (Orion 90-20) containing 10% potassium nitrate in the outer compartment.

Atomic-absorption spectrometer. A Unicam SP 1900 equipped with digital read-out unit, deuterium lamp (SP 1960) and cadmium hollow-cathode lamp was used under the following operation conditions: wavelength 228.8 nm; sensitivity 287; slit-width 104 nm; elevator height 1 cm; lamp current 4 mA; laminar flow burner; air flow 4.5 l./min; acetylene flow 1 l./min.

Spectrophotometer. Beckman DK-2A ratio recording, with 10-mm matched silica cuvettes.

Reagents

All the reagents used were analytical grade, unless otherwise stated, and doubly distilled water was used throughout. Cadmium metal (purity 99.5%, B.D.H.), 0.010*M* EDTA, 0.2% (w/w) pulverized Eriochrome Black T in sodium chloride, 1% aqueous sodium nitrite solution, 1% aqueous ammonium sulphamate solution, 0.2% aqueous *N*-(1-naphthyl)ethylenediamine dihydrochloride solution and stock cadmium chloride solution (Cd 0.1 mg/ml) in 0.05*M* hydrochloric acid were used.

Preparation of samples

Pure powders. Weigh accurately 1 g of the pulverized dried chloramphenicol powder or its ester, dissolve it in the least amount of ethanol needed, transfer to a 100-ml standard flask and make up to the mark with ethanol.

Capsules. Weigh the contents of 20 capsules in a small dish, mix the powder. Weigh a portion equivalent to 2 capsules, dissolve in the least amount of ethanol, filter into a 100-ml standard flask, and dilute to the mark with ethanol.

Suppositories. Dissolve 4 suppositories in the least amount of ethanol, homogenize, transfer to a 100-ml standard flask and make up to the mark with ethanol.

Suspensions. Shake well and transfer 20 ml to a 150-ml stoppered conical flask. Add 50 ml of ethanol, shake for 2 min, leave to stand for 10 min, filter into a 100-ml standard flask, wash and dilute to the mark with ethanol.

Injections. Dissolve the contents of 5 vials in the least amount of water, transfer quantitatively to a 50-ml standard flask and dilute to the mark with water. Shake, and transfer a 10-ml aliquot to a 100-ml standard flask and make up to the mark with water.

Eye and ear-drops. These are usually aqueous solutions containing 0.5–1% chloramphenicol as active ingredient. Such solutions can be used directly without further dilution.

Procedure

Transfer a 1 or 2 ml aliquot of the sample solution to a 100-ml conical flask with a ground-glass neck and a side-arm with bubbler. Add 10 ml of 0.05*M* hydrochloric acid and attach to a water condenser. Heat on a sand-bath while passing carbon dioxide (~ 50 bubbles/min) through the side-arm. When the solution starts boiling, introduce 50–100 mg of cadmium metal turnings, previously washed with 6*M* hydrochloric acid and thoroughly with doubly distilled water, and continue boiling for 15–20 min in a carbon dioxide atmosphere. Cool, transfer the reaction solution to a 50-ml standard flask and make up to the mark with doubly distilled water. This test solution is used for the subsequent measurements. Carry out a blank under similar conditions, without the chloramphenicol sample.

Pure powders or pharmaceutical preparations containing chloramphenicol palmitate, stearate and succinate should be hydrolysed prior to reduction with cadmium metal. An aliquot containing 10–15 mg of the ester is transferred to a test-tube (20 × 2 cm), 1 ml of 1*M* alcoholic potassium hydroxide is added and the mixture shaken for 2 min, then transferred to the reaction vessel; 10 ml of 0.15*M* hydrochloric acid are added and the determination is completed as above.

The reduction products in the final test solution are determined as follows.

Atomic-absorption spectrometric measurement. Transfer a 1.00-ml aliquot of the test solution to a 100-ml standard flask, dilute to the mark with 0.05*M* hydrochloric acid and shake. Aspirate into the air–acetylene flame and measure the absorbance at 228.8 nm. Compare with a calibration graph prepared by treating 0.50–3.00 ml aliquots of the standard cadmium stock solution (0.1 mg/ml) in the same way.

1 mg of Cd ≡ 0.959 mg of chloramphenicol, 1.667 mg of chloramphenicol palmitate, 1.749 mg of chloramphenicol stearate, 1.330 mg of chloramphenicol succinate.

Potentiometric and visual titrations. Transfer a 25.0-ml aliquot of the test solution (≡ 3–7 mg of chloramphenicol) to a 100-ml beaker. Adjust the pH to 10 with aqueous ammonia solution (~ 1 ml of 25% solution). Insert the cadmium ion-selective electrode in conjunction with a double-junction reference electrode, and titrate with 0.010*M* EDTA. Towards the end-point, as indicated by rapid potential jumps, add the titrant in 0.02-ml increments.

Alternatively, add Eriochrome Black T indicator and titrate till the colour changes from pink to blue. Similarly titrate the blank.

1 ml of 0.010*M* EDTA ≡ 1.124 mg of Cd ≡ 1.078 mg of chloramphenicol, 1.484 mg of chloramphenicol succinate, 1.872 mg of chloramphenicol palmitate, 1.965 mg of chloramphenicol stearate.

Spectrophotometric measurements. Transfer a 1.00-ml aliquot of the test solution to a 10-ml standard flask, add 5 ml of 2.5*M* hydrochloric acid and 0.5 ml of 1% sodium nitrite solution, leave to stand for 2 min, then add 2 ml of 1% ammonium sulphamate solution. Leave for 2 min, add 1 ml of 0.2% aqueous *N*-(1-naphthyl)ethylenediamine dihydrochloride solution and shake. After 10 min, read the absorbance at 550 nm (10-mm cuvette) against a blank prepared under identical conditions. Compare the absorbance with that obtained from the mean value of 3 authentic samples of pharmaceutical standard chloramphenicol subjected to the same procedure.

RESULTS AND DISCUSSION

Reaction conditions and products

Reduction of aromatic nitro-compounds by cadmium metal has been little investigated, as far as can be seen from the literature, except for the work of Buděšínský.[22] The reduction of chloramphenicol with cadmium, in acidic media, was therefore examined. The effect of hydrochloric acid on cadmium metal in a carbon dioxide atmosphere was examined by measuring the amount of metal dissolved, the cadmium ion-selective electrode and atomic-absorption spectrometry being used for this purpose. It was found that both the acid concentration and time of reaction affect the dissolution of the metal. Thus on heating cadmium with 10 ml of 0.02, 0.05, 0.1 and 0.2*M* hydrochloric acid under reflux for 15 min, the amount dissolved is 0.1, 0.2, 0.3 and 0.6 mg, respectively. Prolonged heating for up to 30 min does not significantly increase these figures.

The time required for quantitative reduction of chloramphenicol with cadmium metal, in presence of 0.05*M* hydrochloric acid, was investigated by measur-

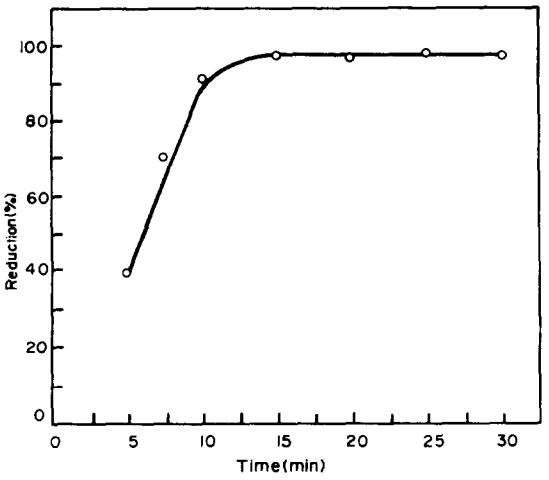
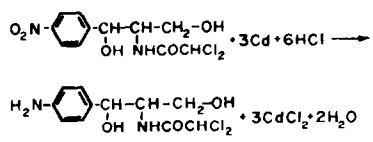


Fig. 1. Effect of time on the reduction of chloramphenicol with cadmium metal in 0.05*M* hydrochloric acid.

ing at intervals, with the cadmium ion-selective electrode, the concentration of the cadmium ions released. Six equivalents of cadmium ion are quantitatively released per mole after 15 min (Fig. 1). Reduction of chloramphenicol stearate, palmitate and succinate esters under the same conditions is not, however, quantitative, probably because these esters exhibit low solubility in aqueous media. Prior hydrolysis, by treatment with 1*M* alcoholic potassium hydroxide at room temperature, leads to complete reduction. The free carboxylate ions released by hydrolysis do not interfere in subsequent measurement procedures.

The reduction product of 0.5 g of chloramphenicol was neutralized with sodium hydroxide, extracted with ethyl acetate, evaporated and crystallized, and its infrared spectrum was examined and compared with that of pure chloramphenicol. The spectrum showed complete absence of the symmetrical and asymmetrical $-NO_2$ stretching bands at 1350 and 1530 cm^{-1}, without any significant changes in the other spectral patterns. Elemental analysis of the product conformed with the formula $C_{11}H_{14}O_3N_2Cl_2$.

These results indicate that chloramphenicol contains no sites other than the $-NO_2$ group available for reduction with cadmium metal, under the prescribed conditions, and the reaction proceeds to completion, ending with the corresponding amine:



When the reaction is conducted in acid of concentration greater than 1*M*, unidentified fragmentation products containing a primary aromatic amine moiety, as confirmed by diazotization and coupling, are obtained.

Measurement by atomic-absorption spectrometry

Determination of the nitro-group in organic compounds by atomic-absorption spectrometry has previously been attempted[23] by reduction to the hydroxylamine derivative with zinc powder and ammonium chloride solution at 95°, followed by reaction of the filtrate with Tollen's reagent. After dissolution of the silver chloride in ammonia solution, the silver metal equivalent to the nitro-group was filtered off, dissolved in nitric acid and measured at 328 nm by atomic-absorption spectrometry. This method, which involves several steps, besides being tedious and time-consuming, is subject to severe interferences by many reducing oxygen, nitrogen and sulphur compounds.

The atomic-absorption spectrometric procedure used in the present work takes advantage of the stoichiometric release of cadmium ions by direct reaction of chloramphenicol with cadmium metal. The reduction solution is diluted with 0.05*M* hydrochloric acid, to bring the final cadmium concentration within the linear range of the calibration graph (*i.e.*, up to 3 μg/ml), and the solution is then aspirated into the acetylene–air flame. The absorbance at 228.8 nm is measured and compared with a calibration graph prepared by use of pure cadmium chloride solution with the same background composition. The results obtained with pure samples of chloramphenicol and its esters in amounts down to 3 mg (Table 1) show an average recovery of 99.5%. The mean standard deviation is ±1.1%.

Measurement by the cadmium ion-selective electrode

Cadmium ions released in the reaction are also measured by potentiometric titration, with the cadmium ion-selective electrode as end-point detector. The pH is adjusted to 10 with ammonia and the sample titrated with EDTA. The results given in Table 1 show an average recovery of 99.3% and a mean standard deviation of ±0.5%. However, direct potentiometric measurement of the cadmium ions in 0.1*M* potassium nitrate as background electrolytes with either a standard calibration graph or the use of the standard addition (spiking) technique, gives inconsistent results with an error of ±3%.

On the other hand, visual end-point detection with Eriochrome Black T as indicator gives results agreeing with the potentiometric values within ±0.03 ml of titrant (≡30 μg of Cd).

Measurement by spectrophotometry

An aliquot of the reduction solution containing 20–200 μg of the reduced chloramphenicol is diazotized and coupled with *N*-(1-naphthyl)ethylenediamine[24] to give an intensely red water-soluble compound with maximum absorption at 550 nm ($E^{1\%}_{1cm}$ = 436). The colour is stable for at least 8 hr and is intense enough to permit the measurement of as little as 20 μg of chloramphenicol per ml of the final test solution. Beer's law is obeyed in the range corresponding to 20–200 μg with an error less

Table 1. Analysis of pure powders of chloramphenicol and its esters by atomic-absorption spectrometry (AAS), spectrophotometry, titrimetry and official procedures

Sample	Recovery, %			Official methods*
	AAS	Cd-electrode	Spectrophotometry	
Chloramphenicol	99.5	99.0	101.1	99.6
	98.1	98.8	100.1	99.4
	99.1	98.3	99.6	97.7
Chloramphenicol	98.9	99.7	100.1	98.0
palmitate	101.2	100.2	98.1	98.7
	100.1	98.9	99.2	99.8
Chloramphenicol	98.6	98.3	98.5	99.6
stearate	100.7	98.9	100.7	98.6
	99.4	99.6	100.1	100.2
Chloramphenicol	98.5	100.1	98.5	98.3
succinate,	98.2	100.1	98.2	98.3
sodium salt	101.1	99.8	101.0	99.5

* British Pharmaceutical Codex procedures[26] were used for the analysis of all the powders except chloramphenicol stearate, which was determined according to the U.S.P. procedure.[25]

Table 2. Effect of some pharmaceutical excipients on the determination of chloramphenicol with the cadmium ion-selective electrode

Excipient	Weight taken, *mg*		Chloramphenicol found	
	Excipient	Chloramphenicol	*mg*	Recovery, %
Acacia	4.7	8.62	8.59	99.6
	3.7	6.66	6.54	99.1
Sucrose	5.2	11.24	11.11	98.8
	3.4	7.84	7.66	97.7
Tween-80	3.7	10.02	9.95	99.3
	4.3	5.38	5.41	100.6
Ethylene glycol	5.4	8.14	8.02	98.5
	4.6	4.87	4.82	98.9
Lactose	3.3	6.54	6.51	99.5
	2.9	7.11	7.15	100.6
Cocoa-butter	5.6	8.88	8.75	98.5
	3.8	5.21	5.06	97.1
Carboxymethyl	3.0	7.82	7.64	97.8
cellulose	4.7	4.41	4.36	98.8
Glycerol	6.3	9.00	8.95	99.4
	3.2	6.73	6.69	99.4
Vanillin	3.9	8.78	8.56	97.5
	7.6	10.71	10.54	98.4

than ±1.5%. Table 1 presents the results obtained with chloramphenicol and its esters; the average recovery was 99.6% and mean standard deviation ±1.0%.

The chloramphenicol and its esters were also assayed by the United States Pharmacopoeia (U.S.P)[25] and the British Pharmaceutical Codex (B.P.C)[26] procedures. The results obtained, as shown in Table 1 (average recovery 99% and standard deviation ±1%), are in good conformity with those obtained by the new procedures. However, the titrimetric procedure surpasses these procedures in precision.

Analysis of pharmaceutical preparations

A number of pharmaceutical additives and diluents commonly used in drug formulations have been examined for their effect on the assay method. Amounts of acacia, sucrose, Tween-80, ethylene glycol, carboxymethyl cellulose, glycerol, vanillin, cocoa-butter and lactose in far greater excess than normally found in oral suspensions, capsules, eye-drops, injections and suppositories were added to both pure chloramphenicol and the blank. No interference was noticed (Table 2).

Determination of chloramphenicol and its esters in various commercially available pharmaceutical preparations was next tried, after suitable dilution to bring their concentration in the test sample within the range 2–15 mg/ml, and filtration to remove insoluble components. The cadmium ions and amine released were measured on each sample by atomic-absorption spectrometry, titrimetry and spectrophotometry. The results obtained with both atomic-absorption spectrometry and spectrophotometry show an average recovery of 98% of the nominal amount, the standard devi-

Table 3. Determination of chloramphenicol and its esters in some pharmaceutical preparations by atomic-absorption spectrometry (AAS), spectrophotometry and potentiometry with the cadmium electrode

Trade name	Source	Nominal amount, as chloramphenicol	Recovery, % U.S.P. Methods[25]	AAS	Cd-electrode	Spectrophotometry
Cidocetine succinate[a] (injections)	CID, Egypt	1 g/vial	96.3	97.2	97.5	97.3
			95.0	96.8	96.9	96.6
Synthomycetine[a] (injections)	Lepetit, Italy	1 g/vial	97.3	96.0	96.4	96.1
			96.6	96.8	96.8	96.9
Levocol[b] (capsule)	NASR, Egypt	250 mg/capsule	100.2	99.1	99.5	100.8
			101.6	98.5	98.8	99.8
Cloramidina[b] (capsule)	ICN ARCO, Switzerland	250 mg/capsule	98.0	95.8	96.4	96.3
			97.2	96.7	87.0	95.7
Cloramidina palmitate[c] (suspensions)	ICN ARCO, Switzerland	25 mg/ml	99.8	100.5	100.0	100.9
			104.2	102.0	99.6	99.0
Miphenicol palmitate[c] (suspensions)	MISR, Egypt	30 mg/ml	100.4	97.0	98.0	98.8
			105.5	98.2	97.5	97.8
Globenicol[b] (suppositories)	Delft, Holand	125 mg/each	100.8	99.8	101.0	98.5
			104.5	100.6	100.0	99.0
Cidocetine[b] (suppositories)	CID, Egypt	125 mg/each	98.3	94.1	95.3	96.1
			101.7	95.3	95.0	95.5
Chloramphenicol[b] (eye-drops)	Alex., Egypt	0.5% aqueous solution	96.3	95.1	96.2	95.8
			94.1	94.8	95.6	96.4
Cidocetine (eye drops)	CID, Egypt	0.5% aqueous solution	104.3	104.3	105.1	104.8
			103.5	104.8	105.8	105.3

The active ingredients are: (a) chloramphenicol succinate; (b) chloramphenicol; (c) chloramphenicol palmitate.

ation being ±2%. Better results are obtained by titration of the released cadmium ions, the average recovery obtained being 98% and the standard deviation ±1.5%. The results obtained by the U.S.P[25] procedures fluctuate, showing a standard deviation of ±3.5%, probably due to extraction, but are within the permissible limit of recovery (*i.e.*, 95–105%).[25,26] The new procedures show greater precision owing to the omission of the prior extraction or separation step.

Advantages

The proposed method, besides its simplicity, offers four advantages: (*a*) at least 4 different measurement procedures can be applied, in parallel, to the same sample; (*b*) no prior extraction of chloramphenicol or its esters is necessary; (*c*) the reagents used are stable enough and need no special precautions during storage or use; (*d*) the results are precise and the accuracy of the outlined procedures is within the permissible limit of the official methods. This renders the method eminently suited to the routine analysis of various pharmaceutical preparations*.

* This work is taken from the Ph.D. Thesis of M. H. Eldesouki (EL-NASR Pharmaceutical Chemical Co., Egypt) and the method described has been satisfactorily used during the last two years for quality control in this company, in parallel with the Pharmacopoeia procedures.

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COMPARATIVE STUDY OF THE MASKING EFFECT OF VARIOUS COMPLEXANS IN THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM WITH ARSENAZO III AND CHLOROPHOSPHONAZO III

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Summary—Results are presented for the masking of 35 elements with the complexans DTPA, EGTA and TTHA in the spectrophotometric determination of uranium(VI) with Arsenazo III at pH 1.8 ± 0.2 and with Chlorophosphonazo III at pH 1.1 ± 0.2. The complexans EDTA and DCTA were found to be less suitable because at low pH they tended to precipitate. DTPA is shown to be especially attractive for masking other elements in the determination of uranium(VI) at low pH.

The bisazo derivatives of chromotropic acid are among the most sensitive reagents for the spectrophotometric determination of uranium.[1-3] Arsenazo III[1,2] and Chlorophosphonazo III,[3] containing arsonic acid and phosphonic acid groups respectively, show the highest sensitivity. For maximum sensitivity with Arsenazo III, uranium should be reduced to the quadrivalent state.[1,2] Unfortunately uranium(IV) is rather unstable and easily oxidized by atmospheric oxygen even in the presence of protective reagents, such as ascorbic acid.[1] Furthermore, trace amounts of zirconium, hafnium and thorium, or scandium, titanium(IV), tin(IV), bismuth, iron(III) and the rare earth elements above certain concentrations interfere and require prior separation. Determination of uranium in its more stable sexivalent state is often preferred as an alternative, because it is only slightly less sensitive. A medium of about pH 2 is used for Arsenazo III and of about pH 1 for Chlorophosphonazo III. Again numerous other elements tend to interfere. One of the best known methods for suppressing such interferences is the addition of EDTA,[2] which forms very stable complexes with many elements, including zirconium, hafnium and thorium, but a relatively unstable one with uranium(VI). The presence of EDTA considerably reduces the sensitivity of the determination of uranium(VI) with Arsenazo III,[3,4] but that of the Chlorophosphonazo III method is much less affected.[3] Furthermore, EDTA tends to precipitate at pH 1–2 and this can introduce complications. Šulcek *et al.*[4] have shown that triethylenetetraminehexa-acetic acid (TTHA) is more favourable than EDTA for masking thorium during the determination of uranium(VI) with Arsenazo III, and Pérez-Bustamante *et al.*[5] have used 1,2-diaminocyclohexanetetra-acetic acid (DCTA) to mask plutonium(IV). Other aminopolycarboxylic acids such as diethylenetriaminepenta-acetic acid (DTPA) and ethyleneglycol-2-(aminoethyl)tetra-acetic acid (EGTA) do not seem to have been investigated as possible masking agents, yet these two reagents complex many elements more strongly than EDTA does, and DTPA has the advantage of being considerably more soluble than either EDTA or DCTA at pH values of about 1–2. In order to establish the merits of these masking agents in the spectrophotometric determination of uranium(VI) with Arsenazo III and Chlorophosphonazo III a comparative study was undertaken, the results of which are presented below.

EXPERIMENTAL

Reagents

EDTA, DCTA, DTPA, EGTA, TTHA, Chlorophosphonazo III and Arsenazo III were obtained commercially. All the reagents were of "*pro analysi*" quality with the exception of TTHA, which was of "*purum*" quality. All other reagents were analytical grade.

Arsenazo III solution 0.05%. Dissolve 100 mg of reagent in 0.25 ml of 1*M* sodium hydroxide and about 60 ml of demineralized water, dilute to about 180 ml, acidify to pH 3–3.5 with 1*M* hydrochloric acid, and dilute accurately to 200 ml.

Chlorophosphonazo III, aqueous solution, 0.025%.

Other reagent solutions. Some of the complexans were supplied in the form of the acids. When solutions were made up, enough sodium hydroxide was added to half-neutralize the acid to make the complexans more soluble and comparable to the disodium salt of EDTA. The final pH-values of the solutions were about 4.

Apparatus

A Zeiss PMQ II spectrophotometer with 1-cm cells was used, and a Metrohm E300 pH-meter.

Procedures

Effect of pH. Five ml of a standard solution containing 50 μg of uranium(VI), amounts of 1*M* hydrochloric acid increasing from 0 to 7.5 ml, 20 ml of 5% DTPA solution (pH 3.9), and 2.0 ml of 0.05% Arsenazo III solution were placed in a series of 25-ml standard flasks. The solutions were made up to volume with demineralized water, and

after 1 hr the absorbance at 655 nm was measured against a series of reagent blanks of similar pH values, but containing no uranium. The blanks were themselves measured against demineralized water. After the absorbance measurements the final pH-values of the solutions were determined.

A similar experiment was carried out with Chlorophosphonazo III, but with 2.0 ml of 0.025% solution of the reagent and measurement at 672 nm. The amount of acid added was extended to 4.0 ml of 5*M* hydrochloric acid.

When the experiments were repeated with the DTPA solution omitted and 2.0 ml of 1*M* sodium acetate added instead, similar results were obtained. Results obtained with the other complexans showed the same general patterns.

Effect of complexans on absorbance. The following reagents were measured into a series of 25-ml standard flasks: 5.0 ml of a standard solution containing 50 μg of uranium(VI); a predetermined volume of 1*M* hydrochloric acid to give a final pH-value of about 1.8; 2.0 ml of 1*M* sodium acetate; 2.0 ml of 5% solution of one of the complexans, leaving one flask without complexan as a control; finally 2.0 ml of 0.05% Arsenazo III solution. The solutions were made up to volume, and after 1 hr the absorbance at 655 nm was measured against a series of similarly prepared reagent blanks containing no uranium. The pH-values of the solutions were then measured.

The experiment was repeated with Chlorophosphonazo III, using only 40 μg of uranium (VI), 2.0 ml of 0.025% solution of the colour-forming reagent, a final pH value of about 1.0 and measurement at 672 nm.

Comparison of masking effect of complexans. In 25-ml standard flasks were placed 40 ml of a standard solution containing 40 μg of uranium(VI) 2.5 ml of 1*M* hydrochloric acid, 2.0 ml of 1*M* sodium acetate and a standard solution containing the element to be masked (in the amount indicated in the Tables). Finally 2.0 ml of 0.05% Arsenazo III solution were added and the solutions were made up to volume. One flask contained all the reagents plus uranium(VI) but no other element. After 1 hr the absorbance was measured at 655 nm. Similar series of solutions were prepared with the following volumes of 1*M* hydrochloric acid and 5% complexan solution: 3.0 ml of acid and 2.0 ml of DTPA (pH 3.0); 3.4 ml of acid and 2.0 ml of EGTA (pH 3.0); 3.0 ml of acid and 2.0 ml of TTHA (pH 3.9). The absorbances of these solutions were measured and the difference from the absorbance of the solution containing all the reagents plus uranium but no other element was calculated.

The whole experiment was repeated with 2.0 ml of 0.025% Chlorophosphonazo III solution as colour-forming reagent, and omission of the 2.0 ml of sodium acetate solution when the complexans were present. The amount of 1*M* hydrochloric acid was 4.0 ml except with EGTA, when only 3.0 ml were used.

RESULTS AND DISCUSSION

Figure 1 shows that the absorbance of the Arsenazo III complex with uranium(VI) is independent of pH only over the rather narrow range of 1.6–2.0. Measurement outside this range is less sensitive and for accurate work requires very careful control of pH. The pH-dependent absorption curve of the Chlorophosphonazo III complex of uranium(VI) has a range of constant absorption between pH 0.9 and 1.3 (Fig. 2). Control of pH outside this range is less critical because the changes of absorbance with pH are considerably smaller, especially in the higher pH range. It was therefore decided to examine the masking effects at pH-values of 1.8 ± 0.2 for the Arsenazo III complex and at 1.1 ± 0.2 for the Chlorophosphonazo III complex.

Because EDTA and DCTA were found to form precipitates when present in about 0.01*M* concentration at these pH-values, they were considered to be less suitable and were omitted from the further study of

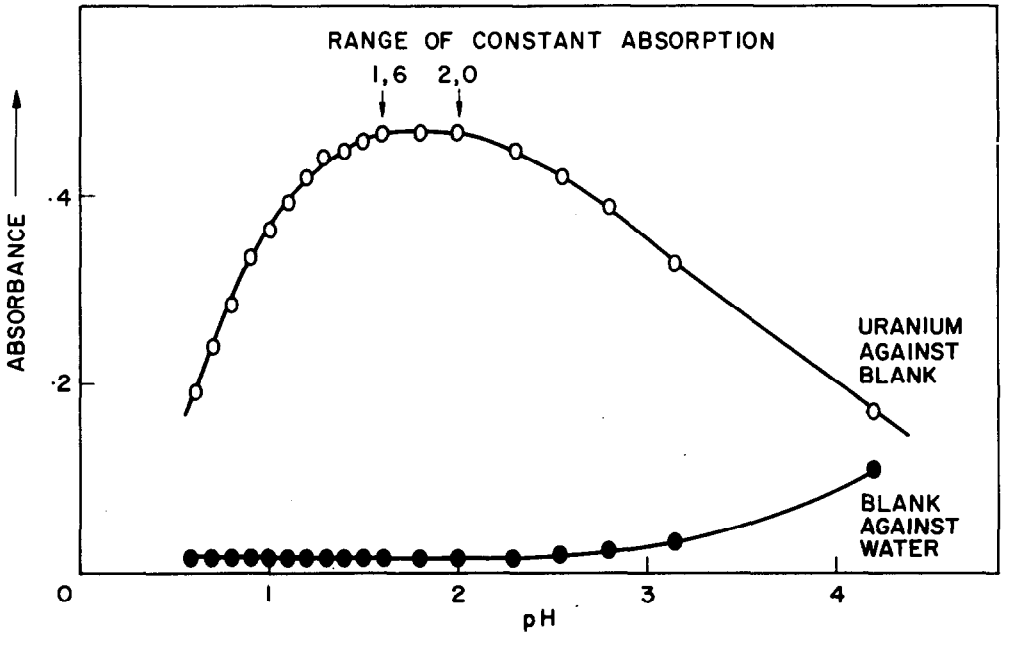

Fig. 1. Absorbance of the complex between uranium(VI) and Arsenazo(III) at 655 nm, as a function of pH (50 μg of U in 25 ml).

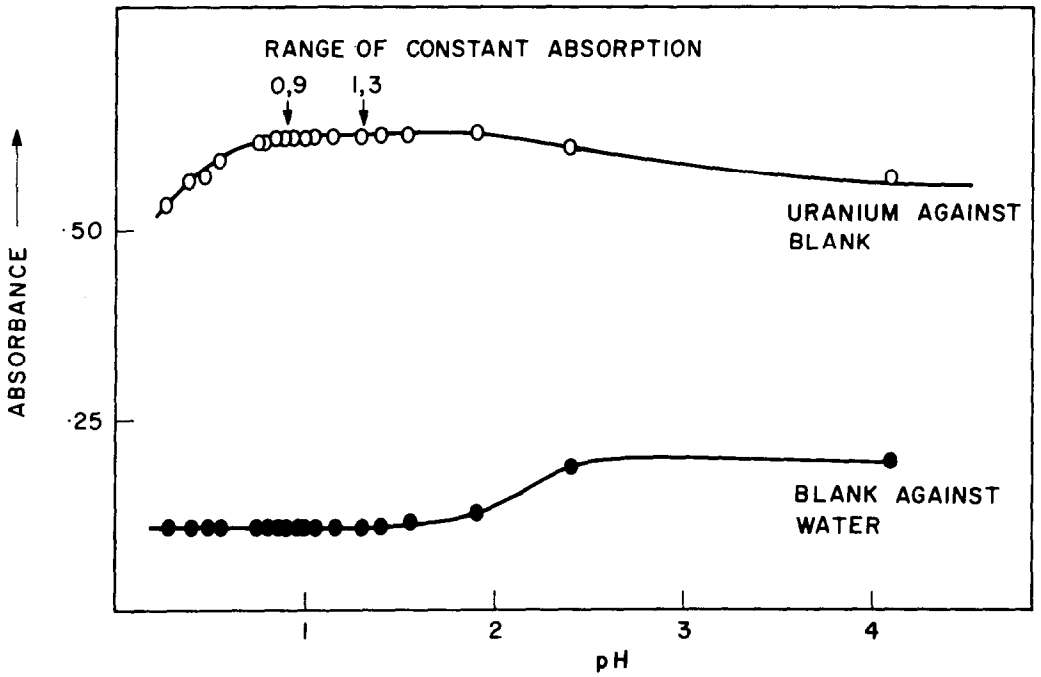

Fig. 2. Absorbance of the complex between uranium(VI) and Chlorophosphonazo III at 672 nm, as a function of pH (50 μg of U in 25 ml).

masking effects. The other masking agents depressed the absorbance by less than 5%.

Arsenazo III

The experimental results are summarized in Table 1. The most strongly interfering elements are Zr, Hf, Th, Sc, Y and the lanthanides. Up to 100 μg of zirconium can be masked by DTPA and up to 20 μg by EGTA and TTHA, while all three complexans are effective in masking 200 μg of hafnium. Thorium cannot be masked completely although TTHA is fairly effective. The interference of 20 μg of scandium can be masked by DTPA and by EGTA but not by TTHA, while yttrium cannot be masked effectively at all. The interference of the light and the heavy lanthanides also cannot be masked completely. Small amounts of gadolinium and erbium can be masked completely, DTPA being the most effective complexan. Bi, Pb, Ga, Fe(III), Sn(IV) and Ti(IV) also interfere fairly strongly in the absence of complexans. Lead(II) in amounts of 1 mg can be masked effectively by DTPA and by TTHA but EGTA is not quite as efficient. The same applies to 200 μg of bismuth. One mg of gallium is masked completely by all three complexans, but only DTPA masks 1 mg of iron(III) effectively, though all three complexans suppress the interference of 100 μg of iron(III). In the case of tin(IV) both DTPA and TTHA mask 1-mg amounts completely, whereas EGTA can only cope with 100 μg. Up to 100 μg of titanium(IV) can be masked by all three complexans. Some elements show relatively weak interference effects in the absence of complexans, *viz.* 1 mg of W(VI), Cu(II), Mo(VI), In, V(IV), Mn(II), Zn or Be. The interference of all these elements [with the exception of copper(II)] can be suppressed completely by all three complexans. However, 100 μg of copper(II) will not affect the absorption of the uranium complex significantly even in the absence of complexans. Quite significant interference is also caused when a niobium solution was added, but this appears to arise more from the tartaric acid in the solution than the niobium. The tartaric acid was added to suppress hydrolysis of the niobium but also complexes with uranium(VI), leading to negative errors. When an attempt was made to use a smaller amount of tartaric acid the final solutions became cloudy because of hydrolysis of niobium, and positive errors occurred.

One-mg amounts of Mg, Ca, Sr, Ba, Co(II), Cd, Ni, Al, Cr(III) and Hg(II) do not interfere to any significant extent ($\leqslant 2\%$ error) in the absence of complexans.

Chlorophosphonazo III

Very strong interference in the absence of complexans is caused by Zr, Hf, Th, Sc, Y and the lanthanides. TTHA masks 100 μg of hafnium and zirconium completely and DTPA masks 20 but not 100 μg of zirconium. It masks 100 μg of hafnium, while EGTA does not effectively mask even 20 μg of either element. The other elements cannot be masked by any of the complexans. It was noted that, even though the deviation from the true result was sometimes small, as for 100 μg of thorium, the colour of the solution was completely wrong and the result fortuitous.

Table 1. Masking effects of complexans in determination of uranium(VI) with Arsenazo III

Other element	Amount, μg	Error for 40 μg of U, %			
		No complexan	DTPA	EGTA	TTHA
Be	100	+0.2	0.0	—	—
Be	1000	+14.5	−0.8	−1.0	−2.5
Mg	1000	±0.0	±0.0	±0.0	—
Ca	100	+0.2	+0.2	+0.2	—
Ca	1000	+2.0	+1.8	+1.8	—
Sr	1000	+0.8	+0.5	+1.0	—
Ba	1000	+2.0	+0.2	+1.5	—
Zn	1000	−14.0	+0.5	±0.0	−0.5
Co(II)	1000	+1.5	+0.5	+0.2	—
Cd	1000	+1.0	+1.0	+1.0	—
Ni(II)	1000	+1.5	+1.8	+1.8	—
Mn(II)	1000	−13.2	+2.0	+2.0	±0.0
Ti(IV)	100	−28.0	−0.5	+0.5	±0.0
Ti(IV)	1000	> −50	> −50	> −50	—
Al	1000	+2.0	+1.8	+1.8	—
V(IV)	1000	+5.5	+1.0	+2.0	+1.5
Cr(III)	1000	+2.0	+2.0	+2.0	—
In	1000	+7.8	±0.0	±0.0	±0.0
Sn(IV)	100	—	—	±0.0	—
Sn(IV)	1000	−31.0	+1.2	−22.0	+0.6
Hg(II)	1000	+1.5	+0.5	+0.5	—
Mo(VI)	1000	+10.8	−0.2	+0.8	−1.2
Cu(II)	100	+0.2	+0.5	+0.8	—
Cu(II)	1000	+3.8	+7.5	+7.5	+8.1
Fe(III)	100	+15.0	+0.5	−0.8	±0.0
Fe(III)	1000	−5.0	+2.0	+10.8	+23.0
Ga	1000	+41.0	+0.5	+0.5	±0.0
Nb*	100	−7.8	−7.5	−9.2	−8.1
Nb*	1000	+4.8	−46.0	—	+26.2
Tl(III)	1000	+14.0	+3.8	±0.0	−2.5
Pb(II)	1000	> +50	+1.8	+3.5	+0.5
Bi(III)	200	+21.0	+0.2	+7.8	+0.5
W(VI)	1000	+4.5	−0.5	+2.2	—
Zr	20	+22.0	+0.2	−0.8	+0.6
Zr	100	> +50	+2.8	+12.5	+7.5
Hf	200	+24.0	+0.2	±0.2	±0.0
Th	20	+24.0	+10.5	+23.0	+5.0
Th	100	> +50	+34.0	> +50	+28.0
Sc	20	> +50	+1.8	+1.5	> +50
Sc	100	> +50	+6.0	—	+16.9
Y	20	+33.0	+4.5	+16.0	+22.0
Y	100	> +50	+22.0	> +50	> +50
La	20	+25.0	+20.0	+14.2	+19.4
Gd	20	+4.0	−0.5	+0.5	+0.5
Gd	100	+8.5	+0.2	+4.5	+1.2
Er	20	+24.0	+1.5	+8.2	+10.0
Yb	20	+22.0	+4.0	+3.8	+26.0
Yb	100	> +50	+6.0	—	—

* Tartrate also present

Some other species such as Pb(II), Cu(II), Ti(IV), W(IV), Mo(VI), Bi, Fe(III), V(IV), Ga, Sn(IV), Ni, Al, Sr, Ba and Ca interfere to a lesser degree when no complexan is present. The interference of 1 mg of W(VI), Mo(VI), Bi, Fe(III), Ga, Sn(IV) and Ni is completely masked by DTPA and TTHA, while EGTA is much less effective and suppresses only the small interference of Bi. Only TTHA suppresses the interference of 100 μg of Ca, Sr, Ba and Al. When 1-mg amounts of these elements are present no complexan completely masks the interference. About 100 μg of Cu(II), Pb(II) and Ti(IV) can be masked by DTPA and TTHA, but EGTA is effective only in the case of copper(II). None of the complexans can cope with 1-mg amounts of lead(II), and only TTHA can mask 1 mg of vanadium(IV).

About 1-mg amounts of Mg, Zn, Co(II), Cd, Mn(II), In, Hg(II), Tl(III) and Cr(III) and 100 μg of Be do not interfere to any significant extent in the absence of complexans. The interference of 1 mg of niobium is also negligible, probably because the lower pH value used with Chlorophosphonazo III suppresses the complexing action of tartrate on uranium(VI) sufficiently.

Table 2. Masking effects of complexans in determination of uranium(VI) with Chlorophosphonazo III

Other element	Amount, μg	Error on 40 μg of U, %			
		No complexan	DTPA	EGTA	TTHA
Be	100	+2.0	+1.5	+1.5	—
Mg	1000	+0.5	+0.5	+0.0	—
Ca	100	+4.8	+3.0	+4.8	1.2
Sr	100	+3.0	+2.5	+2.8	+0.6
Sr	1000	+17.8	+16.0	+18.8	+8.1
Ba	100	+2.8	+2.0	+3.2	+0.6
Ba	1000	+18.5	+13.5	+16.2	+8.8
Al	100	+4.0	+3.5	+4.5	+1.9
Al	1000	+12.5	+11.2	+15.5	+8.8
Zn	1000	+2.0	+1.0	+1.5	—
Co(II)	100	+1.0	+0.5	+1.0	—
Co(II)	1000	+2.5	+2.5	+3.0	—
Cd	1000	±0.0	+0.5	+0.5	—
Ni(II)	1000	+15.0	+1.0	+8.5	±0.0
Mn(II)	1000	+1.2	+0.5	+1.5	—
In	1000	+0.0	±0.0	+0.5	—
Sn(IV)	1000	+5.8	+0.5	+6.0	−1.2
Hg(II)	1000	+2.0	−0.2	−0.5	—
Tl(III)	1000	+0.2	+1.0	+1.5	±0.0
Ga	1000	+19.5	±0.0	+15.0	±0.0
V(IV)	1000	+14.0	+6.0	+14.8	+2.5
Cr(III)	1000	+0.2	+0.2	+0.2	—
Fe(III)	1000	−40.0	+1.0	−21.2	+2.5
Bi(III)	1000	+3.8	±0.0	+1.5	+0.6
Mo(VI)	1000	+10.2	+1.5	+5.0	−0.6
W(VI)	1000	+4.5	−2.0	+4.8	+1.2
Nb*	100	−0.5	±0.0	−0.5	±0.0
Nb*	1000	−1.5	−2.5	−3.0	−2.0
Cu(II)	100	+4.0	+1.0	+1.5	−1.2
Cu(II)	1000	+14.5	—	—	+6.9
Ti(IV)	100	+22.0	−0.5	+3.8	±0.0
Pb(II)	100	+4.8	+1.0	+7.5	+0.6
Pb(II)	1000	+32.0	+13.5	+38.0	+16.2
Zr	20	+4.5	+1.2	+6.0	+0.6
Zr	100	−24.2	+5.5	+5.5	−1.2
Hf	100	−33.0	±0.0	+7.2	+0.6
Th	20	+26.0	+25.0	+26.0	+24.0
Th	100	−4.8	−3.0	+3.2	−4.4
Sc	20	−42.0	−17.5	−5.5	−33.0
Sc	100	−40.0	−42.0	—	—
Y	20	> +50.0	> +50.0	> +50.0	> +50.0
Y	100	> +50.0	> +50.0	> +50.0	—
La	20	+46.0	+47.0	> +50.0	+42.0
Gd	20	+3.0	+2.5	+2.5	—
Gd	100	+10.6	+12.0	+11.5	+11.2
Er	20	> +50.0	> +50.0	> +50.0	+46.0
Yb	20	+40.0	+38.0	> +50.0	+36.0

* Some tartaric acid present.

General aspects

DPTA seems to be the best complexing agent for masking interferences in the determination of uranium(VI) with Arsenazo III at pH 1.8 while TTHA seems to be slightly superior at the lower pH of 1.0 used in the determination with Chlorophosphonazo III. Unfortunately TTHA is very expensive and this prohibits its general use. DPTA is next best and considerably more effective than EGTA. Its price compares with that of EDTA, while its complexes with metals are often considerably more stable. The logs of the overall formation constants for the complexes are: La, 19.5; Cu(II), 21.1; Fe(III), 28.6. These may be compared with 15.5, 18.8 and 25.2 for the corresponding EDTA complexes. In addition pK_3 for acid dissociation of DPTA is considerably lower than the pK_3 for EDTA, DCTA or EGTA. This will favour complexing action at low pH values. Furthermore, probably because of the lower value of its pK_1 (~1.7), DPTA is considerably more soluble in slightly acid solutions than EDTA and DCTA are. It therefore seems to be superior for complexing metals in acid solutions and was found to be especially useful for masking other elements in the spectrophoto-

metric determination of uranium(VI) with Arsenazo III and Chlorophosphonazo III.

The claim[3] that the determination of uranium(VI) with Chlorophosphonazo III is considerably less affected by the presence of EDTA than the determination with Arsenazo III could not be confirmed. Under the conditions used the decrease in sensitivity for both determinations amounted to about 8%. Since precipitation of EDTA was taking place this figure will probably depend on the amount of precipitation and therefore be uncertain, but should be indicative. DTPA, TTHA and EGTA decreased the sensitivity distinctly less than EDTA did, and for this reason also are more attractive.

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SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHATE IONS WITH THE SYSTEM CERIUM(III)–ARSENAZO III

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Summary—A new method for the spectrophotometric determination of PO_4^{3-}, based on the conversion of the complex of cerium(III) with arsenazo III (CeH_4R^-) into $CePO_4$ is proposed and used for the indirect spectrophotometric determination of phosphorus in ferro-silicon. The reaction between Ce(III) and arsenazo III has been studied spectrophotometrically and the stability constants of the complex CeH_4R^- have been determined: $\log \beta_1 = 6.42 \pm 0.10$ (for pH 1–3) and $\log \beta_1 = 6.11 \pm 0.02$ (for pH 5.5–7).

Most spectrophotometric methods for the determination of orthophosphate are based on the formation of heteropoly acids,[1] so it would be useful to have a second method based on a better defined chemical reaction. The complex $CePO_4$ is very stable ($\beta = 10^{18.51}$).[2] This makes possible the indirect spectrophotometric determination of phosphate by the decrease in absorbance of solutions containing less stable coloured complexes of cerium(III). Arsenazo III has been proposed for the spectrophotometric determination of cerium(III) in acid medium (pH about 3)[3] or at pH 4[4] and pH 5.4[5] in the presence of acetate buffer solution. In the last of these, the authors worked with a lower concentration of arsenazo III and established that phosphate interferes with the determination of cerium(III). Although the stability constant of $CePO_4$ is very high, the conditional constant is strongly dependent on pH, and it is therefore necessary to find the conditions under which the $CePO_4$ complex is sufficiently stable relative to the Ce(III)–arsenazo complex for all the phosphate to be bound to Ce(III). The subject of the present paper is to establish the conditions for using the complex of cerium(III) with arsenazo III for the indirect spectrophotometric determination of phosphate.

EXPERIMENTAL

Reagents

Cerium(III), 10^{-2}M. A solution of $Ce(NO_3)_3.6H_2O$ in $10^{-2}M$ nitric acid, standardized complexometrically.[6]

Arsenazo III, 1×10^{-4}M. An aqueous solution, standardized by spectrophotometric titration with thorium nitrate.[7]

Dipotassium hydrogen phosphate, 3×10^{-4}M. Aqueous solution, prepared directly from the dried salt.

Buffers. Nitric acid/potassium nitrate (pH 1–3) and hexamine/nitric acid (pH > 3).

All the reagents used were "pro analysi" grade.

Procedure for ferro-silicon

Dissolve 0.2 g of the sample of ferro-silicon in concentrated nitric acid and hydrofluoric acid. Evaporate to dryness in the presence of sulphuric acid. Cool, take up the residue and dilute to volume in a 50-ml standard flask with ~0.1*M* sulphuric acid. Transfer a 10.00-ml aliquot to a beaker, add 3 drops of 5% potassium thiocyanate solution and reduce iron(III) to iron(II) with ascorbic acid (5% solution, freshly prepared, added dropwise) until the red colour disappears, and then 3–5 drops more. Pass the solution through a cation-exchange column in the hydrogen form, washing the column consecutively with 5 ml of ammonia solution (1 + 10) and 20 ml of distilled water, and collecting the elutate in a 100-ml standard flask. Neutralize the solution to Methyl Orange with hexamine buffer (1*M*, pH 5–5.5) and add 5 ml more, followed by 5.00 ml of $5 \times 10^{-4}M$ cerium(III) and, after 10–15 min, 5.00 ml of $5 \times 10^{-4}M$ arsenazo III. Dilute to the mark with distilled water, and measure the absorbance of the solution at 665 nm.

RESULTS AND DISCUSSION

To define the conditions under which increasing the concentration of phosphate would lead to linear decrease in the absorbance of a solution containing fixed concentrations of cerium(III) and arsenazo III, the mechanism of the reactions must be known. Cerium(III) forms a 1:1 complex with arsenazo III, with two absorption maxima (610 and 665 nm).[3,8] There is no published information about the mechanism of the reaction or the stability of the complex, and different molar absorptivity values have been reported: 4.70×10^4 $l.mole^{-1}.cm^{-1}$,[8] and 6.30×10^4.[3]

As can be seen from Figs. 1–3, in the system cerium(III)–arsenazo III only one mononuclear complex, with one ligand, is formed. The equilibrium is attained within 2–5 min and the absorbance remains constant for several hours.

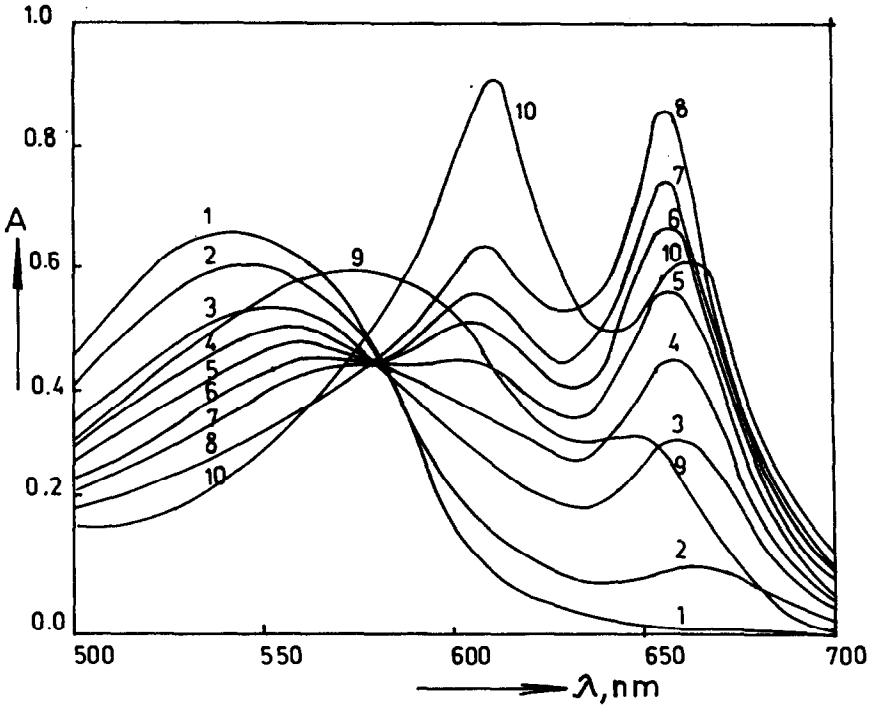

Fig. 1. Absorption spectra, 1-cm cell, pH = 2.75 (curves 1–8), pH = 6.80 (curves 9 and 10), C_A = $1.64 \times 10^{-5}M$ = const. C_{Ce}: 1, 0; 2, 2.00×10^{-6}; 3, 6.00×10^{-6}; 4, 1.00×10^{-5}; 5, 1.40×10^{-5}; 6, 2.00×10^{-5}; 7, 2.60×10^{-5}; 8, 3.50×10^{-5}; 4.40×10^{-5} and 5.50×10^{-5}; 9, 0; 10, $2.00 \times 10^{-5}M$.

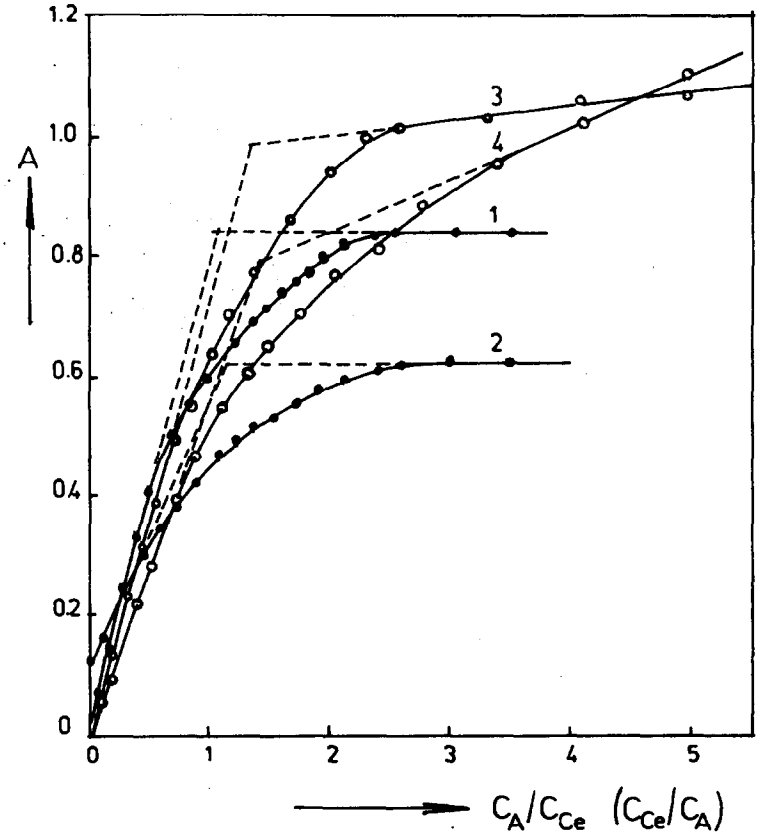

Fig. 2. Mole-ratio method, 1-cm cell, pH = 2.75: 1. $C_A = 1.64 \times 10^{-5}M$ = const., 665 nm. 2. $C_A = 1.64 \times 10^{-5}M$ = const., 610 nm. 3. $C_{Ce} = 2.00 \times 10^{-5}M$ = const., 665 nm. 4. $C_{Ce} = 2.00 \times 10^{-5}M$ = const., 610 nm.

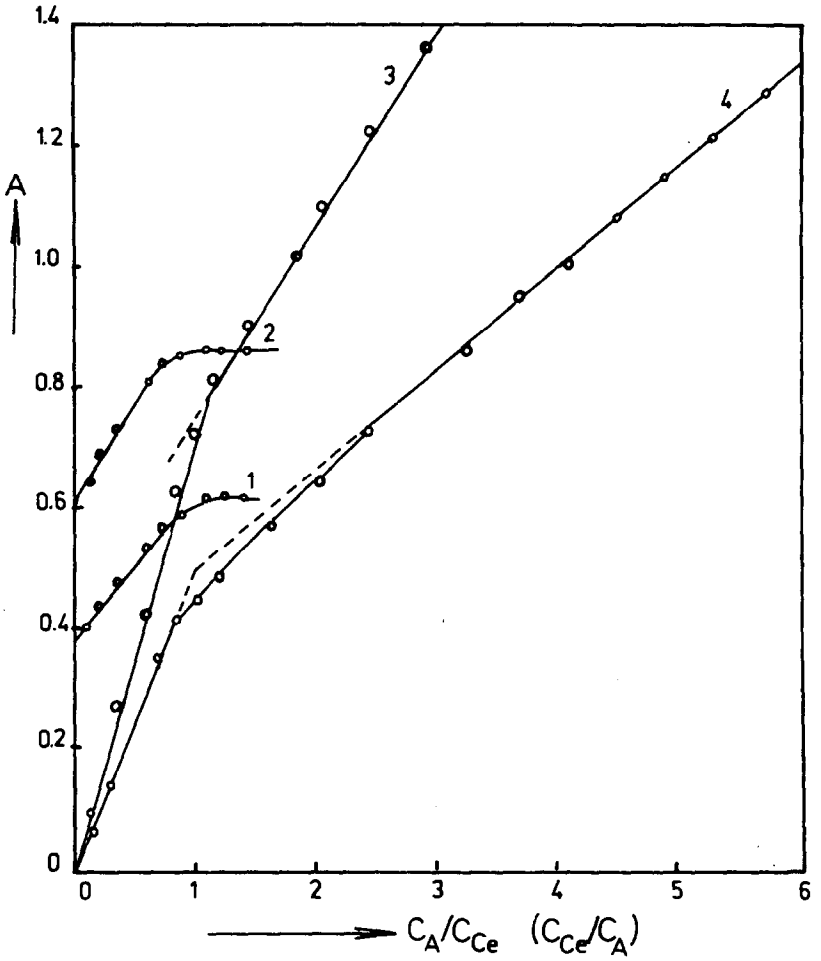

Fig. 3. Mole-ratio method, 1-cm cell: 1. $C_A = 1.64 \times 10^{-5} M$ = const., 665 nm, pH = 6.80. 2. $C_A = 1.64 \times 10^{-5} M$ = const., 610 nm, pH = 6.80. 3. $C_{Ce} = 2.00 \times 10^{-5} M$ = const., 665 nm, pH = 6.80. 4. $C_{Ce} = 1.00 \times 10^{-5} M$ = const., 610 nm, pH = 6.40.

The absorption spectrum of the complex depends on pH in that the more acidic the medium the greater the absorbance at 665 nm compared with that at 610 nm, but at pH > 5 the converse is true. In the two cases the molar absorptivity of the complex is the same whether the metal or the reagent is in excess. At pH > 4.5, the solution becomes opalescent if the [Ce]/[arsenazo] ratio exceeds 3.

At pH < 7 Ce(III) does not form hydroxo-complexes and its interaction with arsenazo III can be written as follows:

$$Ce^{3+} + Ars \overset{K^*}{\rightleftharpoons} CeArs + nH^+ \qquad (1)$$

The number of protons released (n) can be determined from the parameters of the straight line:

$$\log K' = \log K^* + n\text{pH} \qquad (2)$$

where

$$K' = \frac{[CeArs]}{[Ce^{3+}][Ars]}$$

[CeArs] can easily be calculated from the equation:

$$[CeArs] = \frac{A - \epsilon_A C_A}{\epsilon_1 - \epsilon_A}$$

where A is the absorbance measured for total concentrations C_{Ce} and C_A for cerium(III) and arsenazo III respectively, and ϵ_A and ϵ_1 are the molar absorptivities ($1.\text{mole}^{-1}.\text{cm}^{-1}$) of arsenazo III and of the complex respectively.

For the pH-region 1–3, the least-squares method[9] gave the following equation:

$$\log K' = (2.20 \pm 0.19) + (1.27 \pm 0.08)\text{pH} \qquad (3)$$

In a less acidic medium, where the H_4R^{4-} species of arsenazo III predominates, the reaction proceeds without release of protons.

As can be seen from Fig. 4, the interaction between cerium(III), and arsenazo III increases in the pH-region where the H_5R^{3-} species of the reagent appears and predominates. Therefore, equation (1)

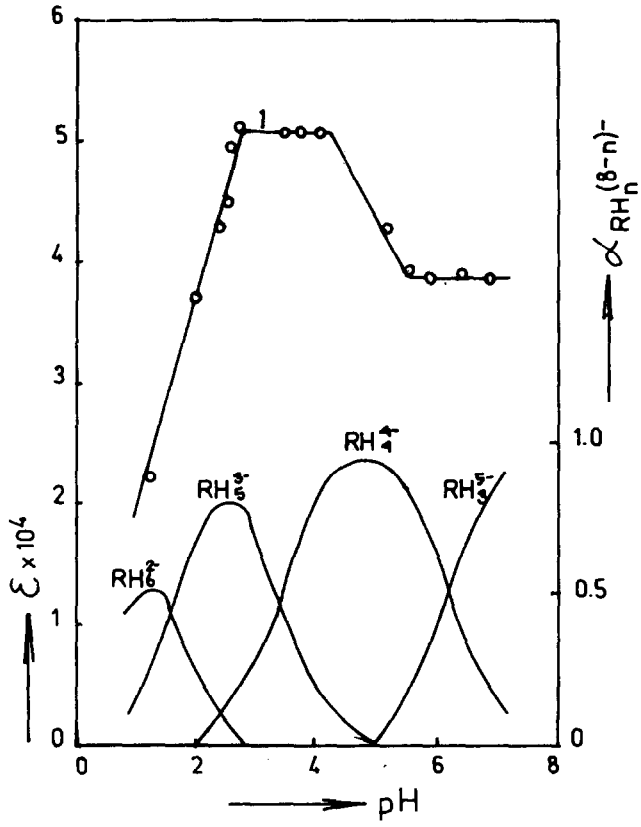

Fig. 4. Molar absorptivity of the complex of Ce(III) with arsenazo III as a function of pH, 665 nm, $C_{Ce}:C_A = 1:3$ (curve 1), and of several ionic species of arsenazo III as a function of pH. The data for the protonation constants of arsenazo III were taken from Buděšínský.[9]

Table 1. Molar absorptivities of the complex CeH_4R^-, $l.mole^{-1}.cm^{-1}$

	565 *nm*	610 *nm*	665 *nm*
pH = 1–3	2.35×10^4	3.87×10^4	5.14×10^4
pH = 5.5–7	2.40×10^4	5.17×10^4	3.76×10^4

Table 2. Values of $\log K'$ and $\log \beta_1$ as a function of pH

pH	$\log K'$	$p\alpha_{H_4R^{4-}}$	$\log \beta_1$
1.40	4.02	2.48	6.50
2.00	4.72	1.60	6.32
2.50	5.26	1.02	6.28
2.65	5.59	0.86	6.45
2.75	5.78	0.76	6.54
3.50	5.23	0.26	5.49
3.70	5.20	0.18	5.38
4.10	5.31	0.08	5.39
5.25	5.46	0.04	5.50
5.50	5.59	0.07	5.63
5.80	5.99	0.14	6.13
5.90	5.92	0.16	6.08
6.20	5.83	0.27	6.10
6.40	5.76	0.37	6.13
6.60	5.62	0.49	6.11

becomes:

for pH = 1–3:

$$Ce^{3+} + H_5R^{3-} \rightleftharpoons CeH_4R^- + H^+ \quad (4)$$

for pH = 5.5–7:

$$Ce^{3+} + H_4R^{4-} \rightleftharpoons CeH_4R^- \quad (5)$$

The complex is anionic and can be extracted with a chloroform solution of hexadecylammonium chloride.

It is of interest that although the complex contains the same species of the reagent, (H_4R^{4-}), the molar absorptivities are dependent on pH (Table 1), but the sum of the values for the two absorption maxima at 610 and 665 nm is almost the same (for pH 1–3, 9.01×10^4, and for pH 5.5–7, 8.93×10^4. The resolution of the spectra into Gaussian curves shows in both cases a third maximum at 17750 cm^{-1} (565 nm).

Table 2 gives the values of the conditional formation constants (K') and of the stability constant (β_1) at different pH-values:

$$\log \beta_1 = \log K' + p\alpha_{H_4R^{4-}} \quad (6)$$

where

$$\alpha_{H_4R^{4-}} = \frac{\beta_4^H[H^*]^4}{1 + \sum_{i=1}^{i=8} \beta_i^H[H^+]^i}$$

and the β_i^H values are the protonation constants of arsenazo III.[9]

The indirect spectrophotometric determination of phosphate is possible when the reaction:

$$CeH_4R^- + PO_4^{3-} \overset{K}{\rightleftharpoons} CePO_4 + H_4R^{4-} \qquad (8)$$

takes place. The dependence of its conditional constant (K) on pH is shown in Fig. 5. The slope of the straight line at pH < 3 is 1, owing to the release of one proton in reaction (4). In this pH-region reaction (8) practically does not take place. The slope of the straight line at pH > 3 is 2, because the phosphate is present as $H_2PO_4^-$. The most convenient pH-value for the determination of phosphate is about 5–5.5, because the molar absorptivity does not depend on pH and the value of K is large enough. When the complex CeH_4R^- is already formed the equilibrium (8) is attained very slowly. That is why the arsenazo III must be added at the end and the absorbance measured after 5–10 min. The concentrations of cerium(III) and arsenazo III must be equivalent or the excess of arsenazo III small, and for the first point of the calibration curve all of the cerium(III) must be bound as CeH_4R^- and $CePO_4$ must be formed only be reaction (8), and not directly.

The equation of the calibration curve calculated by the least-squares method for 665 nm, 1-cm cells, pH = 5.10, $C_{Ce} = C_A = 5 \times 10^{-5} M$ is

$$A = (0.945 \pm 0.007) - (0.620 \pm 0.013)C \qquad (9)$$

where A is the measured absorbance and C is the concentration of phosphorus (ppm).

Equation (9) holds for up to 1 ppm of phosphorus.

CONCLUSION

The sensitivity of reaction (8) allows the analysis of samples containing small quantities of phosphorus, without preliminary concentration. The anions of the most frequently used acids such as hydrochloric, nitric and sulphuric do not interfere. The cations which forms insoluble phosphates or react with arsenazo III will interfere, but these can easily be eliminated with cation-exchangers. We have applied the indirect spectrophotometric method for the determination of phosphorus in ferro-silicon.

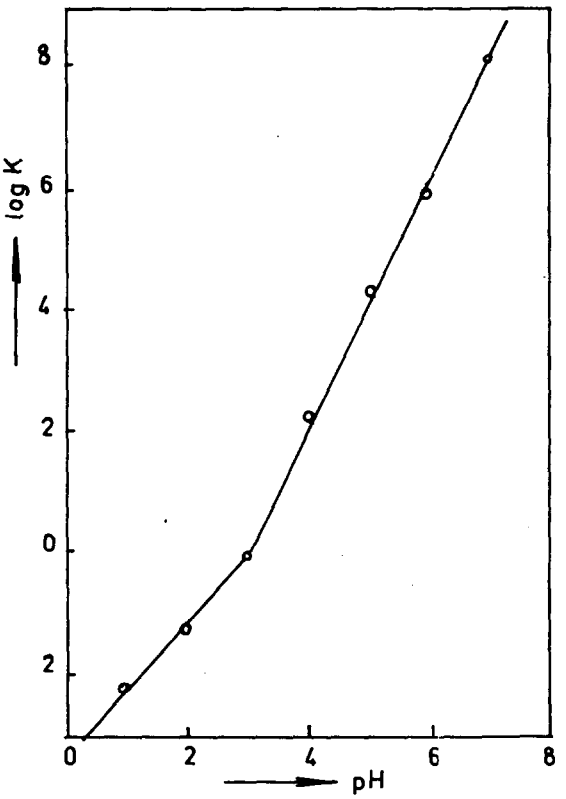

Fig. 5. The equilibrium constant of the reaction of the conversion of CeH_4R^- into $CePO_4$ as a function of pH.

Three standard samples of ferro-silicon were analysed. The results were (0.034 ± 0.002), (0.037 ± 0.002) and (0.041 ± 0.002)%, and the certified values were 0.033, 0.037 and 0.040%, so the method gives satisfactory accuracy and precision.

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SPECTROMETRIC RAPID SAMPLING/MIXING SYSTEM FOR ANALYTICAL/CLINICAL METHODS

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Summary—A rapid sampling/mixing system has been designed which conforms to certain criteria necessary for its use as a clinical analyser. These include low solution volume (< 100 μl) for each determination on a sample, rapid cycle time (< 2 sec to take an aliquot, mix and transfer reactants to an observation cell), good precision (reproducibility better than 0.2%), and ready automation (requiring only two electronic signals to perform a complete cycle). This device has been incorporated into an automated spectrophotometer to be used for a variety of clinical methods. Equilibrium methods for the determination of calcium and albumin are presented that require measurement times of only 6 and 7 sec, respectively. A reaction-rate procedure for total protein is presented that requires only 3 sec per sample. Precisions obtained with these procedures are typically better than 1% in the normal serum range. Results on samples from hospital patients are compared with values obtained on an SMA 12/60 instrument.

The stopped-flow method for rapidly mixing chemical reactants has been shown to be extremely useful for the characterization of many chemical reactions occurring in solution. In recent years a few laboratories have begun to use the stopped-flow technique and modifications of it as a means of automatically and rapidly handling reagents for routine quantitative determinations.

Malmstadt *et al.*[1] determined phosphate in blood serum by monitoring with an automated stopped-flow spectrophotometer the rate of formation of 12-molybdophosphate from Mo(VI) and phosphate. An average of 10 results was obtained on a single sample in about 10 sec with a relative standard deviation of less than 1%. O'Keefe and Malmstadt[2] developed an automated spectrophotometric system which was used for the enzymatic determination of glucose in blood serum. A measurement time of 15 sec resulted in performance of quadruplicate determinations in about 1 min. Glucose concentrations in standards and sera were determined with relative standard deviations of about 1%. Further developments in this system were recently reported[3] and various modes of operation were presented for equilibrium or reaction-rate methods of analysis. Standards and samples were prepared automatically by a solution-handling device based on weight measurement, and sampled automatically by the sampling/mixing module that is presented here. A reaction-rate determination of glucose gave precisions of 0.2–1.3%. Pardue *et al.*[4] have also developed an automated stopped-flow system for equilibrium and kinetic analysis of several analytes in blood serum. Methods discussed include determination of glucose, cholesterol, lactate dehydrogenase and thiocyanate.

A rapid sampling/mixing device has several distinct advantages which make it an attractive addition to a conventional spectrophotometer. The device can dispense reactants very accurately and quickly. It can also mix them and transport the mixture to an observation cell in a very short time. In addition, this technique requires only small solution volumes to obtain quantitative information, through either equilibrium or reaction-rate measurements. However, one of the more significant characteristics of this technique is that with proper controllers the manual handling of reactants is minimized, since the device performs the operations of taking aliquots, mixing and transport. If moderately fast reactions are used, the device can therefore achieve high sample throughput, but even for methods which do not involve rapid reactions, it is reasonable to use this type of device for these key solution manipulations. These characteristics make this technique particularly attractive for laboratories where automated instrumentation, high sample throughput, and low solution volumes are required, such as clinical chemistry laboratories.

A great number of applications of the rapid mixing technique have been devised in many fields of chemistry and biochemistry, but a comprehensive discussion is beyond the scope of this report. A recent review by Crouch[5] on the automated stopped-flow systems used with reaction-rate analytical techniques discusses many analytical applications.

The rapid sampling/mixing technique is gradually gaining recognition as a powerful tool in analytical/clinical analysis because it is applicable and suitable for many types of determination. However, the main

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problem in gaining general acceptability for this technique is that commercial stopped-flow instrumentation designed for rapid kinetic measurements requires the manual opening and closing of several valves, and often requires prohibitively large volumes of solution to rinse the device between samples to eliminate carry-over. Therefore, it is generally not suitable for clinical analyses.

In order to fulfil the needs just described, a rapid sampling/mixing system has been designed which conforms to certain criteria necessary for its use as a clinical analyser. They include low solution volumes (<100 μl) for each determination on a sample, rapid cycle time (<2 sec needed to take an aliquot, mix, and transfer reactants to an observation cell), good precision (reproducibility better than 0.2%), and ready automation (requiring only two electronic signals to perform a complete cycle). This device has been incorporated into an automated spectrophotometer to be used for a variety of clinical methods.

As an illustration of the types of analyses that might be performed with this device, equilibrium methods have been developed for the determination of calcium and albumin and require measurement times of only 6 and 7 sec, respectively. The reaction-rate procedure presented for total protein requires only 3 sec for the determination.

INSTRUMENTATION

The instrumental system used for this work is a modification of systems developed in our laboratories over a period of years and most recently described by O'Keefe and Malmstadt.[2] The system consists of a precision spectrophotometer, a spectrometric rapid sampling/mixing device, and the necessary electronics for interfacing to a minicomputer. The design and construction of the module described here conform to certain characteristics deemed necessary for clinical determinations. To provide flexibility in use and ease of removal for maintenance purposes, the device was designed to fit into a GCA/McPherson sample-cell module.

The rapid sampling/mixing module

A simplified representation of the sampling/mixing module is shown in Fig. 1. In operation, aliquots of sample and reagent are drawn into precision microsyringes. A pneumatic cylinder is used to drive the reagent and sample syringes at sufficient speed to provide rapid mixing as the solutions meet in a specially designed mixing chamber. The pneumatically-actuated valves are used to direct the flow of liquids through the system. The mixed solution flows into the observation cell for measurement by the spectrophotometer. The delivery is terminated by an "End-of-push" signal on the waste syringe, indicating that the proper volumes of liquids have been delivered by the two microsyringes. The system is designed around the recently available line of low dead-volume fluid-handling components for liquid chromatography. These basic components are available from several sources (Pierce Chemical Co., Rockford, IL 61105; Durrum Chemical Corp., Palo Alto, CA 94303; Anspec Co., Ann Arbor, MI 48104; Laboratory Data Control Riviera Beach, FL 33404).

Syringes and holders. Several commercial syringes were evaluated to determine which would require the least maintenance. The best were found to be the Glenco gas/liquid syringe series. The plunger tip consists of a PTFE piece under constant tension from an internal silicone-rubber core to reduce the frequency of leaks.

The Glenco syringe barrels were modified as shown in Fig. 2 to provide a secure mount. The ends of the syringe barrel were cut and polished as shown

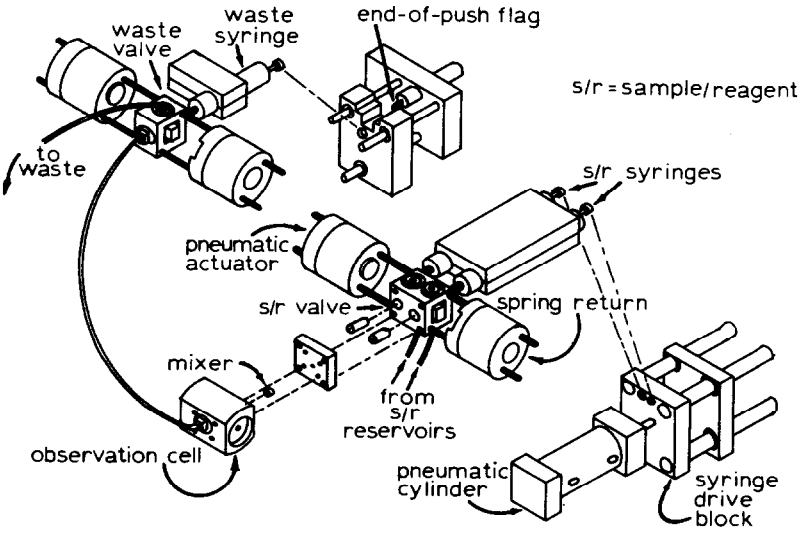

Fig. 1. Schematic representation of the rapid sampling/mixing module.

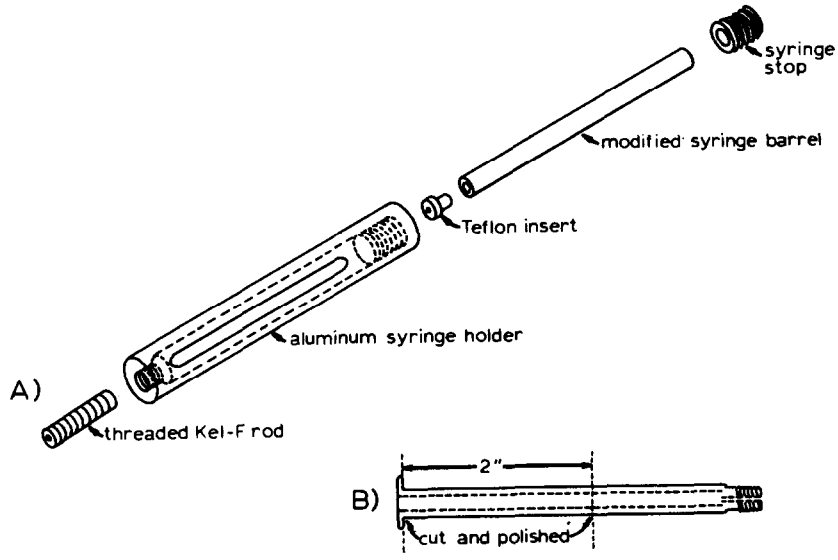

Fig. 2. Details of the syringe holder assembly. (A) Exploded view; (B) modifications to glass syringe barrel.

in Fig. 2B. Care must be taken to ensure that the cut is perpendicular to the syringe barrel. For this particular application the 250-μl syringes (Glenco Model 19925-025) used were cut to a length of 2 in., so that volumes up to 175 μl could be employed. Unimetrics Teflon inserts (Unimetrics Teflon Needle Seals, Model 4042) are pressed into the front end of the syringe barrel to provide a leak-free seal. This syringe barrel is then placed in the aluminium holder.

The holder is made from a $\frac{5}{8}$-in. diameter aluminium rod which has been bored to within $\frac{1}{4}$-in. of the end of the rod to accept the $\frac{11}{32}$-in. diameter syringe barrel. After a syringe barrel has been inserted, the syringe stop is screwed into the back end of the holder, which is tapped to accept 3/8"-24 threads. A 1-in. piece of 1/4-28 threaded Kel-F rod is screwed into the front end of the holder so that it is tight against the PTFE insert in the syringe barrel to eliminate leakage. This rod also provides for attachment of the syringe assembly to the valving system which is described in a following section.

Syringe drive system. The sample and reagent syringes are driven by a double-acting air cylinder (Allenair Type 1 1/8 × 2, Floody Co. Inc., Rockford, IL 61109) which is controlled by two 6-V subminiature solenoid valves (Model 3N06C6, Angar Scientific Corp., Roseland, NJ 07068). This type of driving system was chosen because of flexibility and size compared to spring-loaded or motor-driven devices. Miniature air regulators and gauges (Norgren Model R04-100-RNK-AU and Model 18-013-237, Walter Norris Engineering Co., Chicago, IL 60648) were used to provide approximately 25 psig air-pressure for filling the syringes and 45 psig for the delivery of solutions (which needed to be much faster for efficient mixing of the solutions). Higher pressures decrease the time required to fill the syringes, but also result in occasional degassing of the solutions.

Reagent/sample valving system. This double 3-way valve block contains an inlet port for each of the two syringes just described, an inlet port for tubing which is connected to the sample and reagent reservoirs, and an outlet port for each of the two reactants. The Laboratory Data Control (LDC) pneumatic actuator (Model PA-875), operated by the subminiature solenoid valves described previously, positions the sliders in the valve body at a position so that the syringes are connected to the mixer and observation cell (upon actuation with an 80-psig air-source). The spring return (Model SR1) returns the slider to its normal rest position which again connects the syringes to the sample and reagent reservoirs. A small screw is added to the end of the spring return to allow, in conjunction with an optical interrupter module (General Electric H13B1) monitoring of the valve position (activated or deactivated) as shown in Fig. 3. The necessary electronics for this are described in a later section. This valve block was specially constructed, instead of using two of the commercially available single valves, to provide lower dead-volumes and greater ease of construction of the rest of the module.

The mixing chamber. The mixing chamber used in early studies with this system was purchased from Durrum Instrument Corp., Palo Alto, CA 94303, (Part No. 13072). It is based on a design by Gibson and Milnes[6] and consists of four mixing ports arranged in a counter-tangential fashion to four other ports. Very turbulent mixing is possible within 2 msec in the Durrum instrument.[7] This mixer was found to have a dead-volume of about 40 μl, which seemed rather large for our application, so a different type

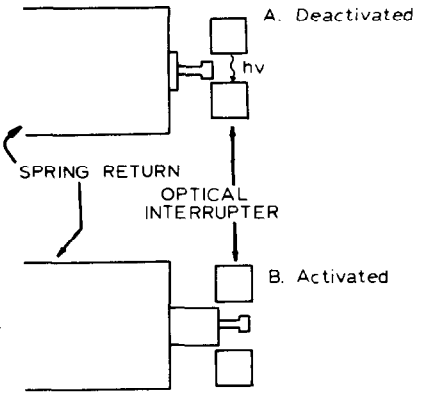

Fig. 3. Encoding scheme for valve position.

was constructed. This new mixer is of the same external dimensions as the Durrum mixer so they are interchangeable. It provides for an "*X*–*Y*" flow for the solutions (*i.e.*, the solutions mix, then are split into two streams, then mixed again) and requires only a 5-μl dead-volume. Mixing efficiency of the two mixers in this sampling/mixing device was found to be essentially identical, so the new version is currently used, to conserve sample.

The observation cell. The observation cell is constructed from a short piece of No. 316 stainless steel ($1\frac{3}{4}$-in. diameter × $1\frac{7}{16}$ in.). A 1.99-mm diameter hole was drilled through the centre and two $\frac{1}{16}$-in. thick quartz plates (Suprasil 2, Amersil Inc., Hillside, NJ 07205) were mounted on either side to provide a 20.0-mm long observation chamber. A hole was drilled in the back end of the observation cell to accept one of the mixers discussed in the previous section. Another hole, opposite this one, was drilled and tapped to accept the 1/4-28 fittings used so that the solution could be easily transported through Teflon tubing to the waste valve.

The waste valve and syringe. A single 3-way valve (LDC Model CAV-3031) was used in conjunction with a pneumatic actuator and spring return for the waste valve. Connected to one of the ports of the valve was the Teflon tubing from the observation cell. Another port was connected to a 1-ml waste syringe (Glenco Model 19925-1), while the third port was connected through a long piece of Teflon tubing to a waste container. The syringe assembly used here was of similar construction to the sample/reagent syringe assemblies. To ease construction and reduce the complexity of the control circuitry, springs were used, rather than a pneumatic cylinder, to drive the syringe plunger. The springs were chosen to provide sufficient force to empty the waste syringe, yet not interfere with it being filled during the delivery cycle of the sample/reagent syringes. The back of the waste-syringe plunger is attached to a block which contains an optical interrupter module (General Electric H13B1). A stationary flag, mounted at a specified distance behind this block is used to provide a signal, "End-of-push", for the termination of delivery (*i.e.*, when the desired volume of reactants has been delivered).

Sequence of operation. In order to help visualize the operation of the device, a typical manual cycle will be described. Details of the electronic controller will then be described. It should be noted that the two signals "Fill" and "Fire" which constitute a complete cycle may originate either from an external device such as a minicomputer or from manual push-buttons on a control box.

When the "Fill" signal is given, the air cylinder is actuated by one of the solenoid valves, resulting in the syringe plungers for the sample/reagent syringes being pulled back to fill the syringes from the solution reservoirs.

Upon receipt of the "Fire" signal several operations occur. The sample/reagent valve and the waste valve are both actuated by two of the solenoid values so that the sample/reagent syringes will be connected to the mixing chamber, observation cell and waste syringe. When both of the valves are in position another solenoid valve actuates the pneumatic cylinder to move it in the direction opposite to that used in the "Fill" operation. The plungers of the sample/reagent syringes are then driven forward at a rapid rate. When the waste syringe has been sufficiently filled, an "End-of-push" signal is generated and the solenoid valves controlling the sample/reagent valve, the waste valve, and the pneumatic cylinder driving the sample/reagent syringes are all deactivated. This provides one complete cycle of the sampling/mixing device. At this point the observation cell contains solution that is isolated from the sample/reagent syringes and the waste syringe.

The time needed to perform the "Fill" operation is approximately 1.2 sec and the "Fire" operation takes about 0.5 sec, resulting in a complete cycle time of less than 2 sec.

Electronic control. The digital and analogue electronics for the control of the sampling/mixing device are shown in Fig. 4 and a parts list is given in Table 1. The resulting waveforms for a complete cycle are shown in Fig. 5. When the sampling/mixing device is in the initial state, $\bar{Q}$ of M1 and Q of FF2 and FF3 are HI, resulting in T1–T4 being turned off. When a "Fill" signal is received by M1, $\bar{Q}$ of M1 goes LO for 1.2 secs, resulting in T1 being turned on, which activates S1 to fill the syringes. When FF1 receives a clear pulse from the "Fire" signal, designated in Fig. 4 as DELIVER, or when PB6 is depressed, G3 goes HI, resulting in FF2 being cleared, which turns on T2 and T3. Activation of solenoids S2 and S3 causes the sample/reagent valve and the waste valve to be actuated. When both valves are completely actuated the light of the optical interrupters is blocked, as previously described, resulting in G7 going LO. This causes G8 and G9 to go HI and G10 to go LO which clears FF3 and turns on S4, the DELIVERY solenoid. This condition holds

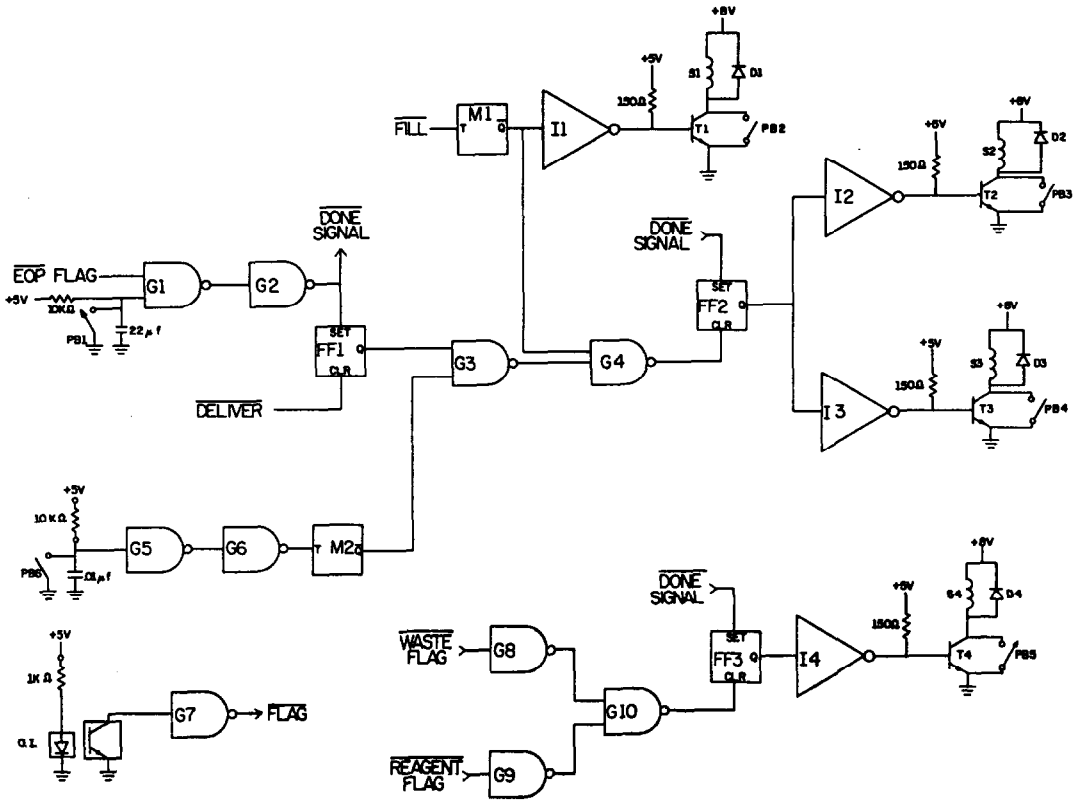

Fig. 4. Control circuitry for the sampling/mixing module.

until an "End-of-push" (EOP) flag is sensed at G1, either by the actual flag, or by the manual simulation push-button, PB1. This results in a LO "Done" signal which sets FF1, FF2, and FF3 causing T2, T3, and T4 to be turned off. The device is now in the initial state and the cycle can be repeated.

Temperature control. Temperature control within the module is accomplished with a proportional heater-controlling device. An air-circulating fan and an 85-W cartridge heater (Model MW-315X-1, Ogden Sales Inc., Arlington Heights, IL 60005) were used in conjunction with a proportional heater-control circuit to keep the module at one of three preset temperatures (25, 30 or 37°C). The control circuit[8] is based upon the SN72440 zero-voltage switch (Texas Instruments Inc.) and controls the temperature of the module to within $\pm 0.1°$ of the set temperature.

Characteristics of the sampling/mixing module. To evaluate the suitability of the sampling/mixing module for use in both reaction-rate and equilibrium measurements, several chemical and physical tests were performed.

Table 1. Parts list for the control circuitry

G1-6,8-10	7400	Quad 2-input NAND gate
G7	74132	Quad 2-input NAND Schmitt trigger
FF1-3	7476	Dual J-K flip-flop
M1, 2	74121	Monostable multivibrator
I1-4	7416	Hex inverter/buffer
T1-4	2N2270	NPN transistor
D1-4	1N914	Signal diode
S1-4	3N06C6	Solenoid (Angar Sci. Corps., Roseland, N.J. 07068)
O.I.	H13B1	Optical interrupter module (General Electric)
PB1, 3-5		Miniature push-buttons and switches for manual control of solenoids
PB2, 6		Miniature push-buttons for "Fill" and "Fire" signals

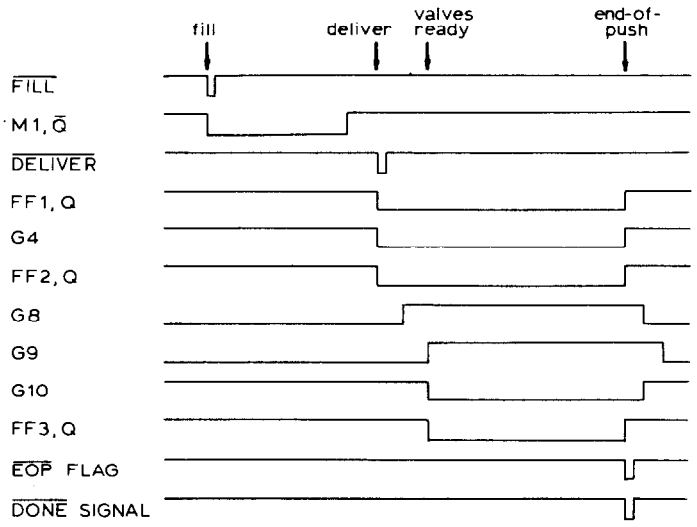

Fig. 5. Timing waveforms generated by the control circuitry.

Determination of dead-time. The dead-time is a measure of the time needed to fill the observation cuvette with a freshly mixed solution. It has been defined as the time needed for the mixed solutions to travel from the point of mixing to the centre of the observation cell.[9] The most common means of measuring the dead time has been the extrapolation method.[9] In this procedure, the course of a reaction is recorded and the resulting rate curve extrapolated back to give the initial absorbance of the reaction mixture if no reaction occurred (*i.e.*, the average absorbance of the two reactants when each is mixed with distilled water). The chemical system used for this determination is based on the reaction of the metallochromic dye, calmagite, with magnesium ions. The reagent composition is similar to that employed in the Pierce diagnostic kit for the determination of magnesium in serum.[10] The reagent consists of 0.18-g/l. calmagite solution (Sigma Chemical Co., St. Louis, MO 63178), 11.9-g/l. Bion PVP solution (Pierce Chemical Co.), 0.13-g/l. Bion NE-9 solution (Pierce Chemical Co.), 3.5m*M* potassium hydroxide, 0.4m*M* potassium cyanide, 0.45*M* potassium chloride, and 0.014m*M* EGTA [ethyleneglycol-bis-(β-amino-ethyl ether)-*N*,*N*′-tetra-acetic acid, Sigma Chemical Co.]. The sample contains 2 ppm magnesium and is

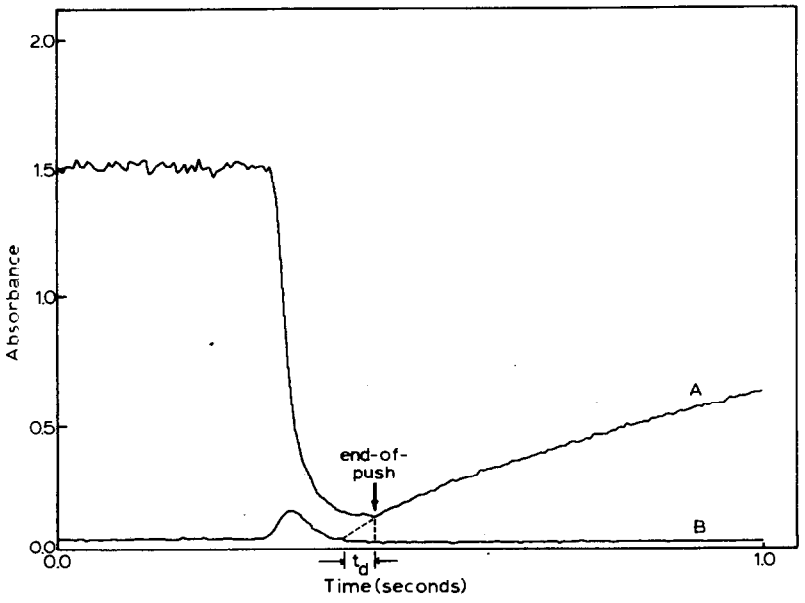

Fig. 6. Formation of magnesium–calmagite complex for determination of dead-time.

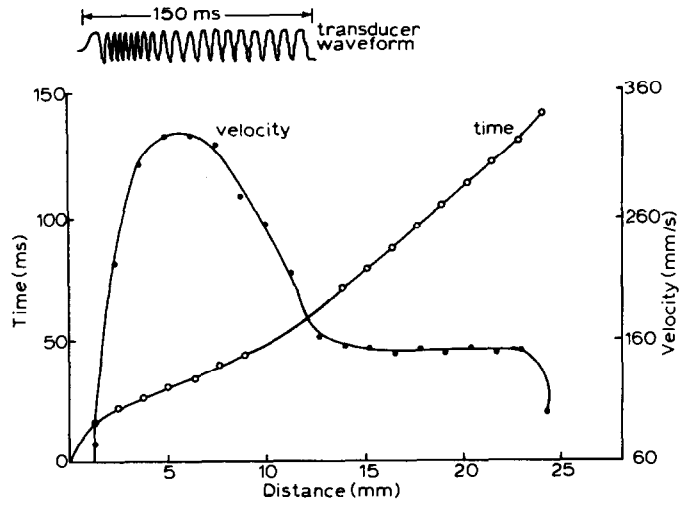

Fig. 7. Dead-time measurements by using velocity transducer on syringe-drive block.

prepared from a stock solution of magnesium nitrate hexahydrate. The resulting curve of absorbance (at 520 nm) *vs.* time is shown in Fig. 6. Extrapolation of the rate curve to the baseline gives a dead-time of 63 msec.

Another procedure for measuring the dead-time is to measure the solution flow-velocity directly. If the dimensions of the channels through which the solutions flow are known it is possible to calculate the dead-time. For this a method similar to that described by Holler *et al.*[11] was used. A transparent ruling, with spacings every 0.05 in., was attached to the syringe-drive block in the module and an optical interrupter module (GE H13B1) was positioned so that the ruling moved through the slot. In order to record the information, a transient recorder[12] similar to that described by Korte and Denton[13] was used, with data being taken at a frequency of 2 kHz. The resulting waveform is shown in Fig. 7 along with the curves for distance *vs.* time and velocity *vs.* time. The dead-time measured by this technique was found to be 62 msec, which is in good agreement with that measured by the other procedure.

Although this dead-time is not comparable to that of commercial stopped-flow devices or numerous research systems,[2,6,7,11] it has proved to be sufficiently low for virtually all applications encountered thus far in our laboratory.

Reproducibility of mixing. To demonstrate the reproducibility of mixing two types of tests were performed. The first involved the measurement of the precision obtained for dilution of a dye. The dye used for this study was an aqueous solution of Blue Dextran 2000 (Pharmacia Fine Chemicals, Inc., Piscataway, NJ 08854) that would give an absorbance of approximately 1 in the observation cell (2-cm pathlength) when mixed with an equal volume of water. Table 2 shows the results obtained for a series of 10 successive cycles of the sampling/mixing module. The relative standard deviation was found to be 0.17% for this dilution study.

The second test involved the reaction of magnesium with calmagite as described in the last section. The same reactants were used and the rate measurements were performed for 2.0 sec following a 0.5-sec delay after mixing. The results are shown in Table 3. These results are essentially identical to those obtained from the dilution study and they both show the excellent reproducibility obtainable with this device.

Volume requirements. The syringes, as described previously, hold a maximum of 250 μl each. However, the stroke allowable in this design (approximately 1.5 in.) limits the maximum delivery to approximately 150 μl per syringe. A more convenient volume has been found to be about 100 μl, which corresponds to a delivery stroke of 1 in. The exact volume requirements were determined by placing the sample and reagent tubes in graduated cylinders and cycling the device 50 times. The volume per cycle was found to be 89 μl for each of the syringes. Smaller volumes could be used, if necessary, to conserve limited

Table 2. Reproducibility of dilution of a dye*

Run	Absorbance
1	0.9294
2	0.9274
3	0.9280
4	0.9316
5	0.9279
6	0.9284
7	0.9315
8	0.9285
9	0.9276
10	0.9301
Average absorbance = 0.9291	
Relative standard deviation = 0.17%	

* Dilution of Blue Dextran solution with water; λ = 620 nm; delay time = 10.0 sec; measurement time = 15.0 sec.

Table 3. Reproducibility of rate measurement*

Run	Rate, $\Delta A/sec$
1	0.2265
2	0.2269
3	0.2263
4	0.2266
5	0.2263
6	0.2264
7	0.2266
8	0.2264
9	0.2267
10	0.2259
Average rate = 0.2264_6	
Relative standard deviation = 0.11%	

* Reaction of magnesium with calmagite; λ = 520 nm; delay time = 0.5 sec; measurement time = 2.0 sec.

samples or reagents. However, the reproducibility obtained may be worse than that shown in the previous section.

Solution carry-over. An important parameter to be considered is the number of flushes needed to change from one solution to another. This is important in terms of both time and reagent conservation. To determine the number of flushes required, the sample tube was placed in a Blue Dextran solution and the device cycled until a reproducible absorbance was obtained. The results are shown in Fig. 8. It can be seen from this figure that by the third cycle the absorbance is within one standard deviation of the final absorbance. Therefore, an accurate measurement could be obtained on the third volume of solution so only 178 μl are required for flushing the system. It should be noted that this volume is highly dependent on the length of tubing used in the device. In this case the tubing length was slightly over 6 in. which is equivalent to about 90 μl, so (as shown in Fig. 8) the first cycle was required just to displace the solution already in the tubing. Longer lengths of tubing would probably require one or more extra flushes, depending on the length.

Spectrophotometer

Light-source and detector system. The spectrophotometer used has recently been described[3] and is similar to that used by O'Keefe and Malmstadt.[2] The main difference is the new sampling/mixing module. The light-source consists of a 6-V, 18-A, tungsten projection lamp (General Electric, Type CPR) and an automatic shutter which can be controlled by an external TTL signal, such as from a minicomputer. The wavelength of interest is selected with a GCA/McPherson EU-700 monochromator (Acton, MA 01720). The sample detector (an RCA 1P28A) is housed in a GCA/McPherson EU-701-30 detector module. A beam-splitter module, also housing a 1P28A photomultiplier tube, is used to correct for any short-term fluctuations in the light-source so that optical information can be obtained on a short (msec) time scale. This module is redesigned from that used previously[2] so that it is mounted directly on the side of the monochromator for stability. A removable lid and a shutter have been added to provide a compartment for the detector that is light-tight even with the lid removed for changing or positioning of the beam-splitter mount. The power supply for the reference photomultiplier tube is the same one as is used for the sample detector. A variable resistor in series with the supply output is used to reduce the gain of the reference detector so that the output currents from the two detectors can be equalized.

Computer. All control functions, data acquisition, data reduction, and display of results were handled by a Digital Equipment Company PDP 8/f minicomputer (Maynard, MA 01754) equipped with 12K of memory and a DEC TU56 dual magnetic tape system for program and data storage. The programs for direct interaction with the spectrophotometer (control

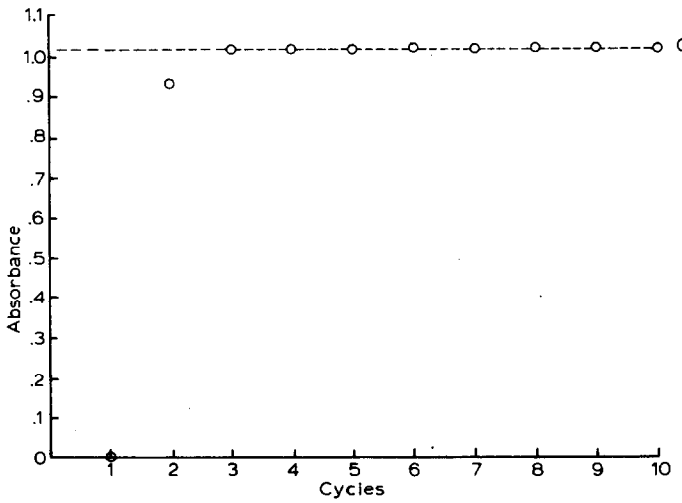

Fig. 8. Solution carry-over of the sampling/mixing module.

functions and data acquisition) were written in SABR, an assembly-level language, while the main programs were written in FORTRAN II under the OS/8 operating system.[14]

Chemical methods

To use the rapid-mixing characteristics of the technique to fullest advantage, the analytical information must be obtained on a reasonably short time scale. However, most analytical methods used in the clinical laboratory are quite inadequate for this technique because of the limitations imposed by the currently existing commercial instrumentation used in their development. If reaction-rate measurements are performed, the rate of reaction in most systems must be slow enough for it to be monitored 15–30 sec after initiation of the reaction. If equilibrium measurements are made, the end-point absorbance must be stable long enough for reliable measurements to be made. Even for the slower methods, however, our new technique can be advantageous since it can automatically provide the solution manipulations required for the reactants, but the full potential of the rapid mixing is not realized until the methods used in the analytical procedures are altered so that they provide adequate information within a few seconds after initiation of the reaction.

To illustrate this, clinical analysis methods for calcium, albumin, and total protein have been developed for use in conjunction with the automated rapid sampling/mixing spectrophotometric system. Considerations in the development of these methods included elimination of as much sample preparation as possible, and utilization of rapid chemical reactions, so that each of the analytical procedures can be performed quickly, to give high sample-throughput. To accomplish this, each of these methods has been modified so that only one serum dilution (1:25) is necessary and only one absorption wavelength (520 nm) is required. Each method has been developed so that a measurement time of less than 10 sec is required to obtain the quantitative information.

EXPERIMENTAL

Standards

Composite standards were used for the determination of calcium, albumin and total protein. The equivalents of 1:25 dilutions of standards containing 50–150 ppm calcium, 31.3–62.5 ppm albumin, and 50–100 ppm total protein were prepared by mixing appropriate volumes of a 100-ppm calcium solution (prepared from primary-standard grade calcium carbonate) and an 8% protein standard solution (Sigma Chemical Co.) and diluting with 0.9% sodium chloride solution.

Samples

Serum samples are diluted 1:25 with 0.9% sodium chloride solution. Each sample is analysed in triplicate for better reliability. These three determinations, in addition to the three cycles normally used for introduction of a new sample into the sampling/mixing module, require about 600 μl of diluted sample. If calcium, total protein and albumin are all determined, a total of 1.8 ml of the diluted sample is required. To ensure an ample supply in case of questionable results, 120 μl of the serum sample is diluted to 3.0 ml with 0.9% sodium chloride solution.

Calcium determination

This procedure is based on the method of Kessler and Wolfman[15] as modified by Moorhead and Biggs[16] in which calcium is complexed with *o*-cresolphthalein complexone in basic solution to form a purple product.

Dye reagent. *o*-Cresolphthalein complexone (Phthalein Purple, Sigma Chemical Co., St. Louis, MO 63178), 0.0375 g, is dissolved in 20–30 ml of water and mixed with 0.85 g of 8-hydroxyquinoline and 2 ml of concentrated hydrochloric acid in 30–40 ml of water, then diluted to 100 ml with water, and stored in a polyethylene container.

Base reagent. Potassium cyanide, 0.25 g, dissolved in 20 ml of water is added slowly to 22.15 g of 2-amino-2-methyl-1-propanol in a 100-ml volumetric flask; this solution is diluted to volume and stored in a polyethylene container.

Working reagent. Equal volumes of the dye and base reagents are mixed and stored in an acid-washed glass container.

Procedure. The sampling/mixing module is used to sample 90-μl volumes of the working reagent and the samples (or standards) and the absorbance of the reaction product at 520 nm is measured during a 1-sec measurement interval, 5 sec after mixing of the reactants.

Results and discussion. Results from a set of working-curve standards are shown in Table 4 and give a correlation coefficient of 0.9997 and a relative standard deviation of 0.2–0.8%. A series of calcium standards was analysed over a period of 5 days to investigate the stability of the reagents and standards. The results obtained are shown in Table 5. With the exception of the first standard, the precisions of the absorbance values measured over this 5-day period are 1% or better. The precision of the slope of the working curve is also 1%. These data indicate that if the same reagents are used throughout, only one working curve needs to be obtained each week.

To check the accuracy of this method a series of commercial control sera was analysed. In addition, serum samples which had been previously analysed on a Technicon SMA 12/60 were obtained from a local hospital. The results obtained are shown in Table 6. The values obtained on the commercial control sera are well within the range of values given by the manufacturers, and results for the hospital samples are in good agreement with the results obtained with the SMA 12/60.

Albumin determination

This method is based on the binding of a dye, Bromocresol Green, by albumin in an acidic solution, as reported by Doumas *et al.*[17]

Dye solution. Bromocresol Green (0.425 g) dissolved in 10 ml of 0.1*M* sodium hydroxide.

Table 4. Results used for calcium working curve*

[Calcium], *ppm*†	Absorbance§	RSD, %
50	0.536	0.8
75	0.681	0.7
100	0.828	0.2
125	0.979	0.5
150	1.142	0.4

* Working curve: slope = 0.0604, intercept = 0.229, r = 0.9997.

† Concentration given is before 1:25 dilution.

§ Average of 3 determinations on a single sample.

Table 5. Day-to-day reproducibility of calcium working curve results

[Calcium], *ppm**	Absorbance† Day 1	Day 3	Day 5	RSD, %
50	0.554	0.539	0.536	1.78
75	0.694	0.694	0.681	1.09
100	0.837	0.829	0.828	0.59
125	0.991	0.984	0.979	0.61
150	1.147	1.143	1.142	0.23
Slope	0.0593	0.0604	0.0604	1.06
Intercept	0.251	0.236	0.229	—
Corr. coeff.	0.9997	0.9996	0.9997	—

* Concentration given is before 1:25 dilution.
† Average of 3 determinations on a single sample.

Table 6. Determination of calcium in control sera and hospital samples

Control sera	Manufacturer's stated value *ppm*	Value found, *ppm*	Difference, *ppm**
ChemTrol			
Normal†	103 ± 3	103	0
Validate§	97 ± 8	101	+4
Calibrate§	105	106	+1
Monitrol I‡	105 ± 3	103	−2
Hospital sample	**SMA 12/60 value, *ppm***	**Value found, *ppm***	**Difference, *ppm****
1	85	86	+1
2	118	116	−2
3	96	94	−2
4	90	90	0
5	97	98	+1
6	100	97	−3
7	101	104	+3
8	85	86	+1
9	91	94	+3
10	98	101	+3

* Value found − value expected.
† Clinton Laboratories, Santa Monica, CA 90404.
§ General Diagnostics, Morris Plains, NJ 07950.
‡ Dade Division, American Hospital Suppply, Miami, FL 33152.

Working reagent. A mixture of 6 ml of 0.53*M* sodium dihydrogen phosphate with 19 ml of 0.11*M* citric acid, 0.35 ml of the dye solution and 2.5 ml 30% Brij-35 solution (Sigma Chemical Co.), stored at 4°.

Procedure. The same procedure was followed as for the calcium determination except that a 2-sec measurement interval was used.

Results and discussion. The results obtained for the working curve standards are shown in Table 7 and give good correlation and precision.

The reproducibility of results on a day-to-day basis was tested by analysing a series of diluted standards over a period of 6 days. By the end of the third day the working reagent had all been used and a new one was prepared and used for two more days on the same set of standards. The results obtained are shown in Table 8. Even though two different reagent solutions were used, the absorbance values of the standards and the slopes of the working curves had precisions of about 3% or better, and the results for days 5 and 6 are much closer than this, indicating that the reagents and standards are stable over several days. Several commercial control sera were analysed, as were the hospital samples already mentioned. The results are shown in Table 9. Very good correlation is found between the manufacturer's values for the control sera and those found by this new procedure. The hospital samples

Table 7. Results used for albumin working curve*

[Albumin], *g/l*†	Absorbance§	RSD, %
31.3	0.299	0.9
37.5	0.350	0.2
43.8	0.412	0.5
50.0	0.470	0.4
62.5	0.586	0.3

* Working curve: slope = 0.0924, intercept = 0.007, r = 0.9997.
† Concentration given is before 1:25 dilution.
§ Average of 3 determinations on a single sample.

Table 8. Day-to-day reproducibility of results with two different working reagents

[Albumin], g/l*.	Absorbance† Day 1§	Day 3§	Day 5‡	Day 6‡	RSD, %
31.7	0.282	0.296	0.303	0.299	3.1
37.5	0.348	0.352	0.353	0.350	0.6
43.7	0.400	0.410	0.424	0.412	2.4
50.0	0.455	0.469	0.482	0.470	2.4
62.5	0.562	0.564	0.591	0.586	2.6
Slope	0.0885	0.0873	0.0921	0.0924	2.8
Intercept	0.011	0.025	0.018	0.007	—
Corr. coeff.	0.9990	0.9982	0.9996	0.9997	—

* Concentration given is before 1:25 dilution.
† Average of 3 determinations on a single sample.
§ First reagent.
‡ Second reagent.

Table 9. Determination of albumin in control sera and hospital samples

Control sera	Manufacturers stated value, g/l.	Value found, g/l.	Difference, g/l.
ChemTrol Normal†	29 ± 3	29	0
ChemTrol Abnormal†	20 ± 1	20	0
Validate§	45 ± 5	44	−1
Monitrol I‡	42 ± 1	43	+1
Hospital sample	**SMA 12/60 value, g/l.**	**Value found, g/l.**	**Difference, g/l.**
1	40	38	−2
2	39	40	+1
3	44	45	+1
4	39	37	−2
5	44	45	+1
6	49	48	−1
7	46	48	+2
8	34	34	0
9	49	50	+1
10	39	37	−2

* Value found − value expected.
† Clinton Laboratories, Santa Monica, CA 90404.
§ General Diagnostics, Morris Plains, NJ 07950
‡ Dade Division, American Hospital Supply, Miami, FL 33152.

also gave good results, and no major differences were noted.

Total protein determination

This method is based on the biuret reaction, in which cupric ions react with the peptide bonds in proteins to form a purple complex.[18]

Working reagent. Solutions of 8.82 g of sodium citrate dihydrate in 20 ml of water, and of 0.75 g of copper sulphate pentahydrate and 1.0 g of potassium iodide in 60 ml of 2*M* sodium hydroxide were mixed together, diluted to 100 ml, and stored in a dark bottle at 4°.

Procedure. The sampling/mixing module is used to sample 90-μl volumes of the working reagent and the samples (or standards) and the rate of change of the absorbance at 520 nm is measured during the first 3 sec of the reaction.

Results and discussion. Table 10 shows the reaction-rate results obtained on a series of standard solutions. The working curve is linear with a slope of 0.0116 and precisions varying from 0.3 to 3.2%. Results were obtained over a period of 5 days to investigate the stability of the standard and reagent solutions. The results are shown in Table 11.

Table 10. Results used for total protein working curve*

[Total protein], g/l.†	Rate, ΔA/sec§	RSD, %
50	0.057	3.2
60	0.069	1.8
70	0.081	0.6
80	0.092	0.6
100	0.115	0.3

* Working curve: slope = 0.0116, intercept = 0.000, r = 0.9999.
† Concentration given is before 1:25 dilution.
§ Average of 3 determinations on a single sample.

Table 11. Day-to-day stability of total protein standards and working reagent

[Total protein] g/l.*	Rate, $\Delta A/sec$† Day 1	Day 2	Day 5	RSD, %
50	0.057	0.058	0.057	1.0
60	0.069	0.069	0.069	0.0
70	0.081	0.080	0.081	0.7
80	0.094	0.091	0.092	1.6
100	0.114	0.114	0.115	0.5
Slope	0.0114	0.0112	0.0116	1.7
Intercept	0.001	0.002	0.000	—
Corr. coeff.	0.998	0.9999	0.9999	—

* Concentration given is before 1:25 dilution.
† Average of 3 determinations on a single sample.

Table 12. Determination of total protein in control sera and hospital samples

Control sera	Manufacturer's stated value, g/l.	Value found, g/l.	Difference, g/l.*
ChemTrol			
Normal†	65 ± 2	65	0
Validate§	65 ± 5	64	−1
Monitrol‡	70 ± 5	67	−3
Hospital sample	**SMA 12/60 value, g/l.**	**Value found, g/l.**	**Difference, g/l.***
1	63	59	−4
2	74	73	−1
3	67	68	+1
4	72	73	+1
5	69	67	−2
6	68	69	+1
7	74	76	+2
8	80	78	−2
9	71	69	−2
10	69	66	−3

* Value found − value expected.
† Clinton Laboratories, Santa Monica, CA 90404.
§ General Diagnostics, Morris Plains, NJ 07950.
‡ Dade Division, American Hospital Supply, Miami, FL 33152.

The precisions of the individual rates vary from less than 0.5 to 1.4% while the precision of the slope of the working curve is 1.6%. These results indicate that the reagent and standards may be used for at least 5 days and that, for the same reagent, only one working curve need be prepared each week.

A series of commercial control sera was analysed to check the accuracy of the method. In addition, the serum samples which had also been analysed on an SMA 12/60 were analysed. The results are listed in Table 12. The results for the commercial control sera are within the range of values given by the manufacturers and the results for the hospital samples are in good agreement with the SMA 12/60 values.

CONCLUSION

The procedures developed for the quantitative determination of calcium, albumin, and total protein have been shown to be precise and accurate, and the reagents and standards are stable over a 5–6 day period. The quantitative measurements at 520 nm can be performed in less than 10 sec for each procedure on a 1:25 dilution of the serum sample. The analysis times for performing these determinations are so short because of the ability to obtain the information much sooner after mixing the reactants than would be possible with manual methods or existing commercial instrumentation.

Thus, the rapid sampling/mixing spectrophotometric system can have high sample-throughput as well as high precision and is a useful tool for routine use in the clinical laboratory.

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HANDLING OF ELECTRONIC ABSORPTION SPECTRA WITH A DESK TOP COMPUTER—I

A FULLY AUTOMATIC SPECTROPHOTOMETRIC TITRATION SYSTEM WITH ON-LINE DATA ACQUISITION

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Summary—A fully automatic system for combined spectrophotometric and pH titrations with on-line digital data acquisition is described for a Cary 118C spectrophotometer. The system consists of a temperature-controlled titration cell, a motor burette, a digital pH-meter, and an HP9820 desk-top computer. The computer controls the stepwise addition of reagent, the wavelength and paper drives, and the recorder pen; the absorption data and the pH-values are obtained on-line. A special interface was constructed from CMOS components. This is compatible with other computers or microprocessors having the necessary input/output facilities. The performance of the system has been tested critically. In 50 min more than 200 data points, each representing the mean of ten individual readings, can be collected, and the number of data points which can be obtained in one run is practically unlimited. The system avoids the cumbersome and error-prone manual handling of a large amount of data, it saves time, and, most important, the results have a high reproducibility.

In principle, spectrophotometry between 200 and 800 nm is one of the most general methods for the analysis of multicomponent mixtures of weak acids or of co-ordination compounds in solution since most species show some typical absorption in this range. Nevertheless, some serious difficulties have to be overcome if useful results are to be obtained in any but the simplest and most favourable cases.[1–3] The problems arise (*a*) from the extensive overlap of spectra of related species in equilibrium mixtures and (*b*) from the strong correlation between the molar absorptivities and stability constants of minor species. Difficulties from (*a*) can be reduced by extending the study to more wavelengths, at the expense of an increasing number of unknowns and data points. Correlation between stability constants and molar absorptivities is more tricky to deal with if there is no means of converting minor into major species by changing the experimental conditions. Experimental errors, particularly in the absorbance A, become decisive in this situation. It has been shown, for instance, that absorbance errors as small as 0.003 could lead to completely erratic results, whereas synthetic data with an uncertainty of ~0.0001 could be analysed satisfactorily.[2] It is difficult, if not impossible, to avoid introducing errors of the order of 0.1–0.2% simply by repositioning the absorption cell after a change of sample and by reading the results off the usual chart recordings.

It follows that the analysis of multicomponent mixtures by spectrophotometry necessitates the handling of a fair amount of extremely precise raw data. Also, simplifications in the numerical treatment of the data must be kept to a minimum and an estimate of the uncertainties of the parameters obtained is essential. Obviously this task is best solved by a digital computer and several specific[5,6] or general[7,8] programs for the calculation of equilibrium constants from spectrophotometric data, on medium or large computers, have been described.

With the availability of efficient and comparatively inexpensive microcomputers, on-line data acquisition[9,10] has become possible even in laboratories without access to big computer systems,[11,12] thus eliminating time-consuming and error-prone manipulations such as digitizing the chart recordings. Here we describe an arrangement which permits completely automatic spectrophotometric titration of 2–2.5-ml samples in standard 1-cm glass or quartz cells, measures the absorbance with high precision ($\sigma_A < 0.0002$ absorbance units) at up to 30 wavelengths, and stores the data on magnetic tape for later numerical treatment.

EXPERIMENTAL

The *spectrophotometric titration unit* consists of a temperature-controlled cell adapter A for the cell compartment of a Cary 118 C spectrophotometer*. For concomitant

* We thank Mr. W. Arnold for the construction of the titration unit.

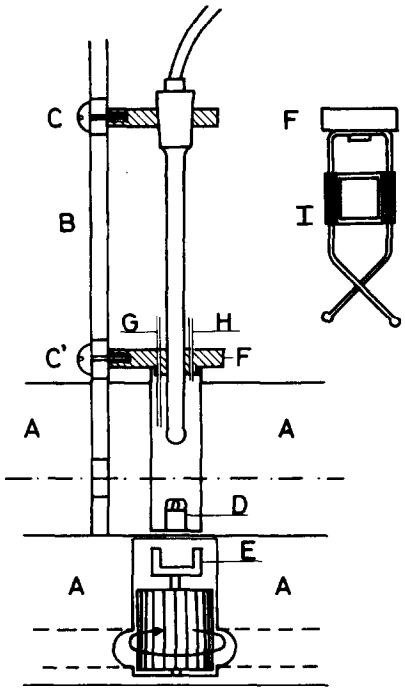

Fig. 1. Unit for combined spectrophotometric and pH titrations. A: temperature-controlled cell adapter; B: glass electrode adapter; C,C': adjustment screws; D,E: magnetic stirrers; F: cell-holder with springs I; G: titrant line; H: nitrogen inlet.

measurements of pH, the adapter B can accept a combined glass microelectrode (Metrohm EA125). The optimum position of the cell and the electrode can be fixed by the screws C and C'. Stirring is effected by a small Teflon-coated magnetic stirrer D which is activated by the magnet E driven by the circulating water of the thermostat (Haake NBS). The cell is covered by a Teflon cap F with holes drilled for the glass electrode and the polyethylene tubes for addition of titrant (G) and flushing with nitrogen or another gas (H). It is held in place by a pair of springs I fastened to F. The standard cover of the cell compartment is replaced by a cylindrical cover 15 cm high and 11.5 cm in diameter. The electrode cable and the polyethylene tubes for titrant and nitrogen (0.05 mm bore) are introduced into the cell compartment through suitable holes drilled in the vertical front plate of the spectrophotometer. Titrant is delivered in portions of 0.01 ml from a 1-ml motor burette with a tantalum plunger (Metrohm E 415/E 552). Ideally an initial volume of 2.3–2.5 ml is treated with a total volume of 0.2–0.3 ml of titrant, but up to 0.5 ml, allowing 50 equidistant titration steps, can be added. A similar but more complicated cell for spectrophotometric titrations has been described.[13] The main differences of that system are: (1) the absorption cell, a special polypropylene construction with quartz windows, is not available commercially, (2) titrant is added manually from a micrometer syringe and no provision is made for on-line data acquisition.

The *interfacing* of the Cary 118 C with the HP 9820 desk-top computer is outlined in Fig. 2. The HP 9820 (439 registers of memory) is equipped with a peripheral control block PC II, cassette memory 9865A, a general input/output interface HP 11202A, and two BCD input interfaces HP 11203A. One of the BCD interfaces is connected to the digital panel meter of the Cary 118 C, the other to the BCD output of the pH-meter (Metrohm E 500).

For the computer control of the spectrophotometer and the motor burette, the HP 11202A interface is used along with block PC II. This allows the conversion of denary numbers into binary numbers and their transfer to peripheral instruments. The computer has to update the digital voltmeter (BCD output of the Cary 118 C), drive the chart-paper and wavelength-stepping motors, actuate the pen, and control the motor burette. The set of commands used is summarized in Table 1. Some of these (6–15) have to be stored, but others (1–5, 16) are needed only as pulses, *e.g.*, to drive the stepping motors (WTB 1,1; WTB 1,2; WTB 1,3; WTB 1,5). Two commands are available to activate the wavelength-stepping motor. While WTB 1,1 will effect one single step (0.005 nm), 20 consecutive steps are performed at the maximum speed of the spectrophotometer (1000 steps per second) by WTB 1,5.

Since the HP 11202A interface provides the necessary control signals only as short pulses, a special interface had

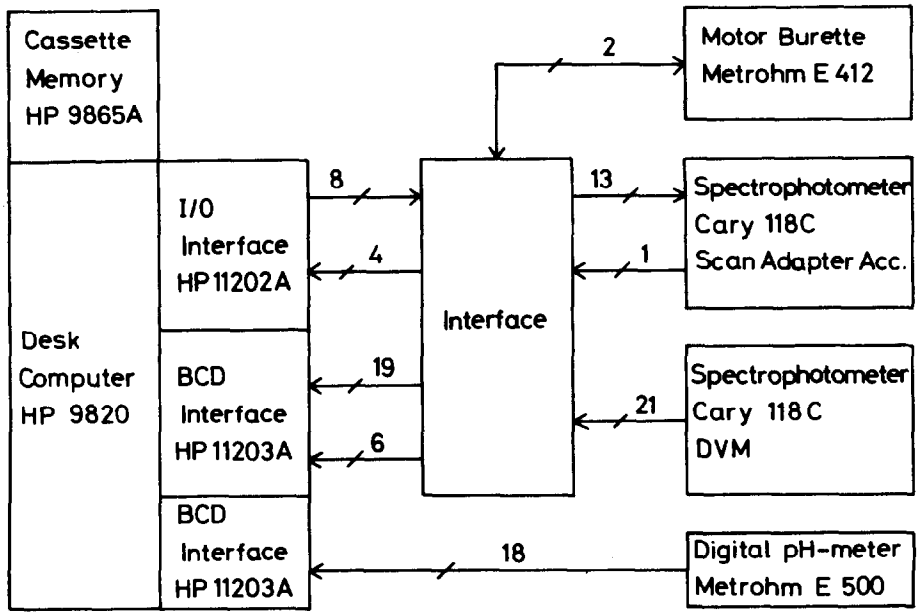

Fig. 2. Block diagram of the fully automatic titration system.

Table 1. HP 9820 commands for the control of the Cary 118 C spectrophotometer and the motor burette

HP 9820 commands*	Functions of the special interface	Signals of Cary scan adapter accessory
WTB 1,0	Reset all catches	—
WTB 1,1	External scan clock pulse	EXSCP
WTB 1,2	External chart clock pulse	EXCCP
WTB 1,3	External chart and scan pulse	EXCCP + EXSCP
WTB 1,4	External clock pulse	EXCP
WTB 1,5	20 times EXSCP	—
WTB 1,6	Actuate motor burette (0.01 ml)	—
WTB 1,7	Scan off	SCOF
WTB 1,8	External control enable	EXTC
WTB 1,9	External clock pulse enable	EXCO
WTB 1,10	Scan in plus direction	SCAP
WTB 1,11	Scan in minus direction	SCAM
WTB 1,12	Pen down	PEDN
WTB 1,13	Pen up	PEUP
WTB 1,14	Hold reading command	HOLD
WTB 1,15	Reading absorbance enable	—

* It is assumed that the HP 11202A interface is set to select code 1.

to be developed to store and transfer the commands. This additional interface has been built into, and is powered by, the Cary 118 C. Because of the high power requirements of TTL integrated circuits, which could not be met directly by the electronics of the spectrophotometer, low-power CMOS integrated circuits were used instead. In order to switch the TTL circuits of the HP 11202A and the DTL circuits of the Cary 118 C (scan adapter accessory Cary 01-857105-00), buffers were needed.

Data acquisition by means of the HP 9820 desk-top computer with cassette memory and expansion to 435 registers can be made very flexible. One of the main characteristics of our program* for combined spectrophotometric and pH-titrations is that human interference has been excluded wherever possible. The program starts by searching for the next empty file on the cassette. Thereafter, initial values of ligand and metal ion concentrations and volume are read in, followed by the longest (initial) wavelength, the wavelength decrement, the shortest wavelength, the chart setting in nm/in., the increment of titrant (in multiples of 0.01 ml), and the total volume of reagent, in that order. In a modification of the program, the total volume of reagent may be subdivided into two portions with different increments. After setting the spectrophotometer to the initial wavelength, the computer reads in the baseline. The pen is lowered for scanning in the minus direction (from long to short wavelength) and raised when the direction is reversed, monochromator and chart paper are driven to the specified points and the absorbance values are read in. Noise is reduced by taking the average of a suitable number (usually 10) of individual readings at each wavelength. After reading in the baseline the computer returns to the initial wavelength and stops to allow the cell content to be changed. The rest of the procedure is completely automatic. The pH-value is read in and printed together with the amount of titrant added. When the absorbance at the last wavelength has been measured, the specified amount of reagent is added, the monochromator and the chart paper are reset to the initial values, and the procedure above is repeated. When (*a*) the specified total amount of titrant has been added or (*b*) the storage capacity of the calculator is exhausted, a file of adequate length is labelled and the data are recorded on the tape. In case (*a*) the job is terminated and the file and cassette numbers are printed for later identification. If (*b*) was the reason for the data transfer, a continuation label is set before storing the data, and the computer resumes its job. In this way, the number of data points which can be collected by the program is practically unlimited. At present, numerical treatment of the data is done on an HP 9821 calculator with fully expanded memory (1446 registers) and the programs can handle up to 30 absorbance curves at up to 30 wavelengths. Computational details will be described in Part II of this work.[14]

In spectrophotometric titrations which do not need measurements of pH, essentially the same data acquisition program is used. Reading of pH values is omitted, of course, and zeros are filled into the corresponding data registers in order to keep the file structure identical in all cases, to allow the use of the same main programs for numerical treatment of both types of data.

* Listings of the program and details of the interface circuitry are available on request.

RESULTS AND DISCUSSION

The performance of the system has been tested and compared with the electronic stability of the spectrophotometer. Shot noise and electronic drift have been examined at 550, 700 and 800 nm with the cell compartment empty and a zero offset of about 0.08 absorbance units. At each wavelength 10 measurements were taken at maximum speed (α) and at 1-min intervals (β). The series were repeated five times over a period of 1.5 h. The results are collected in Table 2, where the standard errors of the means of ten measurements (1), indicating shot noise and/or short-term drift are compared with the standard deviations between individual batches (2), corresponding to long-term drift.

$$SE = \sqrt{\frac{\sum_{i=1}^{N} A_i^2 - \left(\sum_{i=1}^{N} A_i\right)^2 / N}{N(N-1)}} \qquad (1)$$

where A_i = individual absorbance readings, N = number of readings ($N = 10$).

Table 2. Shot noise and electronic drift of the Cary 118 C

Wavelength, *nm*		550	700	800
Shot noise, range of	α*	2–3	2–5	1–5
$SE \times 10^5$, equation (1)	β*	2–5	2–5	2–3
Long term drift,	α	2	6	6
$SD \times 10^5$, equation (2)	β	3	3	2

* α: values obtained at the maximum speed of the system.
β: individual readings at 1-min intervals.

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \bar{A}_i^2 - \left(\sum_{i=1}^{n} \bar{A}_i\right)^2 / n}{n-1}} \qquad (2)$$

$\bar{A}_i$ = mean of N readings, n = number of batches ($n = 5$)

As can be seen from Table 2, the uncertainty in absorbance arising from electronic instability is always below 0.0001 units if the average of 10 readings is taken. No significant difference is observed between measurements at maximum speed (α) and at 1-min intervals (β). The long-term stability of the instrument is excellent, since the standard deviations *SD* (2) obtained from five different batches closely correspond to the standard errors *SE* (1) of the means of ten individual measurements, which indicates that electronic drift does not play a significant role.

In the measurement of stirred solutions additional effects are unavoidable. These were studied between 700 and 800 nm by using Cu^{2+}/EDTA in borate buffer as a chemically stable test mixture. All solutions were filtered through Millipore filters RAWP 01300 (pore-size 0.0012 mm) before use. The solutions were (*a*): $[Cu^{2+}] = 0.008M$, $[EDTA] = 0.01M$; (*b*): $[Cu^{2+}] = 0.0016M$, $[EDTA] = 0.002M$; (*c*): $[Cu^{2+}] = 0.004M$, $[EDTA] = 0.005M$; all in $0.1M$ borate buffer, pH = 9.0. Throughout, $0.1M$ borate, pH 9.0, was used as the reference.

Ten spectra were run for solutions (*a*) and (*b*) and absorbances were read at 10-nm intervals, the average of 10 successive readings being taken as the raw data. This gives a total of 1100 absorbance readings per solution (*a*) or (*b*). The time needed for such an experiment is 25 min. The effect of dilution was studied by adding to (*c*) $0.1M$ borate, pH 9.0, in 20 steps of 0.02 ml. The results obtained for (*a*), (*b*) and (*c*) at 700 and 800 nm are compiled in Table 3 and were rather similar to those at the other wavelengths. No erroneous signal was recorded during the entire experiment.

As expected, and as can be seen from Table 3, the introduction of stirred solutions into the light-path increases the experimental uncertainty. Besides chemical instability, which should not play a role in our test system, evaporation of the solvent and the presence of turbidity from minute particles have to be considered. The former is the major source of errors unless the cell is carefully sealed. In an experiment corresponding to (*a*), but with no special precautions against evaporation, the absorbance increased steadily at the rate of 0.8% per hour. Slow evaporation from stirred solutions is difficult to avoid completely, of course, but no significant time-dependence was observed in the experiments summarized in Table 3 and we assume that turbidity is the main source of error in these cases.

As can be seen from Table 3, the standard deviations *SD* (2) of the absorbances are all between 0.0001 and 0.0002 units, irrespective of the total absorbance. Therefore absorbance values near 0.5 are obtained with an error of about 0.03% and even at 0.05 total absorbance the relative standard deviation is less than 1%. It can be seen from Table 3, (*c*), that this situation does not change significantly when an actual titration is performed. At 800 (700) nm, the values $A_0 = 0.2864 \pm 0.00006$ (0.3548 ± 0.00007) and $A_r = -0.0074 \pm 0.0006$ (-0.0089 ± 0.0007), shown with their standard errors, have been calculated from equation (3) for this last experiment. The values for A_0 indicate the likely uncertainties for the absorptivities in well-behaved systems.

$$A = A_r + A_0 v_0/(v_0 + v_t) \qquad (3)$$

A_0 initial absorbance; A_r absorbance at infinite dilution; v_0 initial volume; v_t volume of titrant added.

With the system described in this paper a large number of high-precision data from spectrophoto-

Table 3. Performance of the titration system

Wavelength, *nm*	Solution (*a*)*	(*b*)*	(*c*)†
700	0.68007	0.12728	—
	±0.00016	±0.00015	±0.00014
800	0.54536	0.15462	—
	±0.00012	±0.00017	±0.00016

* Mean absorbance, with standard deviation, *cf.* equation (2).
† Standard deviation of A_r from equation (3).

metric titrations can be obtained easily in a short time. Reading absorbances from normal chart paper can be done at best with an uncertainty of 0.2% which is about one order of magnitude worse than that achieved here. The application of general non-linear least-squares programs developed for the numerical treatment (with a desk-top calculator) of spectrophotometric titrations involving acid–base and complex equilibria will be described in Part II of this work.[14]

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MULTIPARAMETRIC CURVE FITTING—IV

COMPUTER-ASSISTED ESTIMATION OF SUCCESSIVE DISSOCIATION CONSTANTS AND OF MOLAR ABSORPTIVITIES FROM ABSORBANCE–pH CURVES BY THE DCLET PROGRAM

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Summary—The program DCLET evaluates the dissociation (or protonation) constants and molar absorptivities ϵ_{H_jL} of all light-absorbing species H_jL, ($j = 0,\ldots, J$) of a polyprotic acid H_JL by a non linear regression of the function $A = f(\text{pH}; \text{p}\bar{K}_a, \bar{\epsilon}_{H_jL})$, i.e., by multiparametric curve fitting. The three specific subroutines DATADC, UBBEDC, SKRDC described form part of the general program ABLET. The goodness of fit is tested by statistical examination of the residuals. Heuristic or algorithmic strategies of minimization may be used, and experimental or synthetic data may be processed. By examining the effects on the results of varying the density and distribution of points of a synthetic data set, it is possible to improve the planning of experiments, and by introducing parametric weight, to improve the sensitivity of a particular parameter in a model.

Existing methods for determination of dissociation constants by various approaches have already been discussed comprehensively.[1–5] For a protolytic system in which some species have characteristic absorption spectra in the ultraviolet and/or the visible region, a spectrophotometric method can be used with advantage. A sufficiently large set of experimental data can readily be obtained by microtitration combined with simultaneous monitoring of pH.[6–10] For monoprotic systems, the normal graphical procedure involves transformation of the experimental absorbance–pH function.[2] A straightforward numerical version based on this approach makes use of simple linear regression.[11,12]

The methods proposed for determining values of two successive dissociation constants usually require knowledge of the absorptivities of the two boundary species of the protonation system. The best values of the other parameters are then calculated by successive approximation. Irving, Rossotti and Harris[13] have presented a method which may be used even if the molar absorptivities of individual species cannot be determined directly. Thamer and Voigt[14] have developed a method which is applicable where the ratio of the dissociation constants is less than 10^3. In a subsequent paper, Thamer[15] outlined two general methods of calculation for two close successive dissociation constants, which do not require the determination of absorptivities. Both the direct approach and the calculation by successive approximation are designed for a desk calculator; however, they are rather tedious and susceptible to arithmetical errors. Roth and Bunnett[6] have expressed the absorbance–pH function as a linear equation in five unknowns. A suitable selection of five points is made from the experimental A–pH graph to obtain a set of five simultaneous equations which is solved by a computer. This method, like that of Thamer,[15] has the disadvantage that all the other experimental points are ignored.

The Taylor's-series approximation in non-linear least-squares analysis has been adapted by Auld and French,[8] with the use of an electronic desk calculator, to allow the dissociation constants for a monoprotic and a diprotic acid to be calculated even when the constants are similar. Heys, Kinns and Perrin[17] have described an approach in which all the experimental data are used to find the best fit for the molar absorptivity of the intermediate species and for K_{a1} and K_{a2} by a least-square minimization method. The A–pH function is rewritten to obtain an expression in three unknowns. For each of n experimental points an equation is obtained and the set of n simultaneous equations is solved by a matrix transposition technique using the IBM library subroutine[18] based on the method of Golub.[19] Multiparametric curve-fitting can also be used in combination with deviation-pat-

Part III, *Sb, Věd. Pr., Vys Šk. Chemickotechnologická, Pardubice*, 1978, **39**, 41.

tern recognition to distinguish the titration curve of a diprotic species with close dissociation constants from that of a monoprotic system.[20]

During the sixties various non-linear estimation methods were developed and applied to the calculation of equilibrium constants.[2-5,21] Multiparametric least-squares curve-fitting programs for laboratory minicomputers,[22,23] recently described, have been used for various analytical purposes, including the evaluation of rate and equilibrium constants.[24] The pit-mapping program LETAGROP VRID by Sillén *et al.*[25,26] offers perhaps the most comprehensive approach to the computation of the stability constants. On the other hand, the transfer of a large program of this type, such as SPEFO,[26] to a large computer requires much effort. Two programs, FA608 and EY608, designed by Kankare[27] for small computers (16 kbyte) can evaluate equilibrium constants and their errors for multicomponent systems, from spectrophotometric data. Factor analysis is used to estimate the number of independently varying components, and for data reduction. Molar absorptivities of individual components are also calculated and spectra interpolated from these values can be plotted. Kaden and Zuberbühler[28] have published a general program capable of processing either potentiometric or absorbance data by changing one or two subroutines. By systematic computer analysis of spectral data, the number of absorbing species, the stoichiometry, and the equilibrium constants or acid dissociation constants of Pyrocatechol Violet, and of the system tin(IV)–Pyrocatechol Violet were determined by means of a program written by Wakley and Varga.[29] The program SQUAD, written by Leggett and McBryde,[30] is capable of calculating, simultaneously or individually, acid association constants (and hence pK_a values) and overall stability constants (of the concentration type) for any species formed in systems containing up to two metals and two ligands.

This paper deals with computation of both distinct and similar dissociation constants from absorbance–pH data. The program DCLET is based on the subroutine LETAG,[31-33] which is a version of Sillén's LETAGROP VRID, adapted to be used with the subroutine LETAG.

THEORY

Equation of an absorbance–pH curve

The spectrophotometric determination of dissociation (or protonation) constants of a polyprotic acid H_jL is based on the interpretation of the absorbance–pH curve measured over the pH range covering the main regions of existence of all the species of interest. The equation for the A–pH curve is written in the following manner

$$A = d(\epsilon_L[L] + \epsilon_{HL}[HL] + \epsilon_{H_2L}[H_2L] + \ldots) \quad (1)$$

where d is the path-length and ϵ_L, ϵ_{HL}, ϵ_{H_2L}, ... *etc.* are the absorptivities of those species of the protonation system which absorb light at the chosen wavelength. Each equilibrium concentration of a species which occurs to a measurable extent within the pH range of interest is a function of the hydrogen-ion activity.

Since

$$[H_jL] = c_{H_jL} \cdot \beta_{H_jL} \cdot a_{H^+}^j / (1 + \beta_{HL} \cdot a_{H^+} + \cdots + \beta_{H_jL} \cdot a_{H^+}^j)$$

and

$$\beta_{H_jL} = [H_jL]/[L] \cdot a_{H^+}^j,$$

where c_{H_jL} is the analytical concentration of acid H_jL, equation (1) may be written as

$$A = dc_{H_jL} \frac{\epsilon_L + \epsilon_{HL}\beta_{HL}a_{H^+} + \epsilon_{H_2L}\beta_{H_2L}a_{H^+}^2 + \cdots}{1 + \beta_{HL}a_{H^+} + \beta_{H_2L}a_{H^+}^2 + \cdots}$$

$$= dc_{H_jL} \frac{\epsilon_L + \sum_{j=1}^{J} \epsilon_{H_jL} 10^{(j \cdot \log a_{H^+} + \log \beta_{H_jL})}}{1 + \sum_{j=1}^{J} 10^{(j \cdot \log a_{H^+} + \log \beta_{H_jL})}}. \quad (2)$$

In the expression $j \cdot \log a_{H^+} + \log \beta_{H_jL}$, the conventional activity pH scale ($pH = -\log a_{H^+}$) may be used and the protonation constant β_{H_jL} may be expressed as a function of the mixed stepwise dissociation constant $K_{ai} = a_{H^+}[H_{i-1}L]/[H_iL]$:

$$j \cdot \log a_{H^+} + \log \beta_{H_jL} = \sum_{i=1}^{j} pK_{ai} - j \cdot pH \quad (2a)$$

In many practical cases the protonation equilibria are sufficiently separated, ($pK_{a(j-1)} - 3 \leqslant pK_{aj} \leqslant pK_{a(j+1)} + 3$) for each of them to be treated as a monoprotic system, in which case equation (2) can be written as

$$A = dc_{HL} \frac{\epsilon_L + \epsilon_{HL} 10^{(pK_{a1} - pH)}}{1 + 10^{(pK_{a1} - pH)}}. \quad (3)$$

If a graphical approach is used,[1] equation (3) is usually put in the linearized logarithmic form

$$\log \frac{A - dc_{HL}\epsilon_L}{dc_{HL}\epsilon_{HL} - A} = pK_{a1} - pH \quad (4)$$

and the value of pK_{a1} is found as the point where the straight line intersects the pH-axis.

Regression analysis

In the analysis of an absorbance–pH curve in terms of equation (2), it must be remembered that the values of the parameters ϵ_{H_jL} and pK_a are known only approximately from the graph, but by means of the following refinement process their exact values can be determined.

For fitting the non-linear function [equation (2)], a least-squares curve-fitting method seems to be the

Table 1. Example of the use of program DCLET. Experimental data set for Pyrocatechol Violet: absorbances measured at 590 nm, $c_L = 3.0 \times 10^{-5} M$ (output shortened and simplified)

Data

Number of points	23
Total concentration of dye (M)	1.00000
Coefficients Q_1, Q_2	1.0 1.0
WT (Temperature, K)	298.16
WW [Liquid-junction potential correction (mV)]	0.0
WZ (pa_H of standard buffer solution)	7.413
WK [Nernstian slope of glass electrode (mV)]	57.59

i	pH_{read}	$pa_{H+,i}$	$A_{exp,i}$
1	4.220	4.133	0.008
2	5.300	5.242	0.019
3	6.490	6.465	0.101
4	6.800	6.783	0.169
5	7.020	7.009	0.246
6	7.200	7.194	0.326
7	7.480	7.482	0.479
8	7.600	7.605	0.546
9	7.800	7.811	0.665
10	8.050	8.067	0.793
11	8.200	8.221	0.862
12	8.350	8.376	0.907
13	8.740	8.776	0.957
14	8.960	9.002	0.952
15	9.160	9.208	0.916
16	9.370	9.423	0.858
17	9.600	9.660	0.783
18	9.790	9.855	0.710
19	10.040	10.112	0.606
20	10.250	10.327	0.535
21	10.500	10.584	0.472
22	10.790	10.882	0.425
23	11.220	11.324	0.389

Leta

Values of parameters during minimization process

	ϵ_L	ϵ_{HL}	pK_{11}	ϵ_{H_2L}	pK_{21}	U
Initial guess	0.389	1.000	9.800	0.008	7.600	3.7954E-02
After 1st iteration	0.363	1.064	9.854	0.018	7.581	7.2909E-04
After 2nd iteration	0.366	1.067	9.835	0.020	7.589	6.3589E-04
After 3rd iteration	0.366	1.067	9.835	0.020	7.589	6.3588E-04
After 4th iteration	0.366	1.067	9.835	0.020	7.589	6.3587E-04
After termination	0.36633	1.06713	9.83496	0.01969	7.58880	
	+ −	+ −	+ −	+ −	+ −	
	0.00461	0.00519	0.01480	0.00343	0.00871	

SIGY (standard deviation of absorbance) = 0.0059

Skrik

Curve fitting analysis by statistical test of residuals, $\delta_i = (A_{exp,i} - A_{calc,i}) \times 10^4$

i	δ_i	i	δ_i
1	−121	21	−2
2	−54	22	10
3	81	23	6
4	75		
5	79		
6	54		
7	0		
8	−67		
9	−75		
10	−74		
11	25		
12	30		
13	20		
14	59		
15	1		
16	−45		
17	4		
18	31		
19	−21		
20	−17		

Statistical parameter

Arithmetic mean 1.7E-07
Mean deviation 4.1E-03
Standard deviation σ 0.0053
Variance σ^2 2.8E-05
Moment coefficient of skewness −0.369
Moment coefficient of kurtosis 2.51
Observed χ^2 2.39
[χ^2 (6; 0.95) should be less than 12.6]

most convenient; thus the sum of the squares of the residuals

$$U = \sum_{i=1}^{N} w_i(A_{exp,i} - A_{calc,i})^2 \qquad (5)$$

for N experimental points $\{A_{exp}, pH\}$ is minimized. The statistical weight, w_i, is usually set at unity for experimental data sets, but for synthetic data sets the weight is calculated, and is different from unity. Nonlinear estimation is a problem of optimization in multiparametric space, in which the values of A and pH are the given numbers and the parameters ϵ_{H_jL}, $pK_{a,j}$ are the variables. Starting from an initial guess of the values of the parameters, the "best" values are reached by a few successive approximations. If it is assumed that the error-square sum U is a second-degree function of m parameters, then $0.5(m+1)(m+2)$ points in parametric space suffice for calculation of the position of the minimum.

Successful application of this computational method depends on the use of the heuristic (trial-and-error) minimization process and also on the number of data available. An accurate, well-planned A–pH data set should be obtained, and the measurement should be properly conducted (*e.g.*, a combined pH–photometric microtitration technique seems to be best[10]). The number of protons taking part in the protonation equilibria within the relevant pH range should be known so that a suitable mathematical model may be chosen. The data should first be treated graphically to detect and eliminate possible systematic errors and to obtain initial guess for the parameters to be determined.

COMPUTER PROGRAM

The program DCLET is written in Fortran and has been run on an EC 1040 (Robotron, GDR) which is compatible with the IBM 360 computer. Some of the basic subroutines of the minimization process will be published in another paper from this series.[33] An older version of DCLET (1972) for a smaller store-capacity computer (Hewlett-Packard 2116, Tesla 200), called JDC-LETAG, is available on request.

The program will accept up to 90 points from the A–pH curve, and 7 unknown parameters (*i.e.* $J \leqslant 3$ in H_JL). The program has a flexible structure allowing a heuristic (trial-and-error) strategy to be used in the minimization process.

Program DCLET starts with initial guesses of the parameters from the data, *i.e.*, experimental values of the independent variable pH_i and of the dependent variable A_i. A "best" approximation to the unknown parameters (pK_a, ϵ_{H_jL}), and their standard deviations (σ_{pK_a}, $\sigma_{\epsilon_{H_jL}}$) are calculated. The agreement between the calculated A–pH curve and the experimental points can be seen in a table. The residuals (*i.e.*, the differences between the experimental and calculated absorbances) are analysed statistically.

If the model is satisfactory, and there are no systematic errors in the data, the residuals should have a Gaussian distribution with the following properties: arithmetic mean zero, standard deviation σ, mean deviation $(\sqrt{2\pi})\sigma \approx 0.8\sigma$, variance σ^2, moment coefficient of skewness zero, and moment coefficient of kurtosis 3.[34] A value for χ^2 is then derived from the difference between the observed and calculated probability. A fit can be accepted at the appropriate confidence level if the observed value of χ^2 is less than the theoretical value.

The program may be used to study minimization strategy, and to plan experimental work. For this, a synthetic data set simulating an A–pH curve in which the points are loaded by calculated errors, is generlated for each point of an A–pH curve. Thus, it is possible to increase the influence of each parameter values of the independent variable, pH, it is possible to find an optimum plan for an experiment. The structure of the program allows a weight to be calculated for each point of an A–pH curve. Thus, it is possible to increase the influence of each parameter on the value of the error-square sum.

The program consists of a main program and several subroutines. The subroutine DCLET allows the user to read the data, to call another subroutine for a simulation of synthetic data, if desired, for the minimization process, and for output. The subroutine DATADC does all the calculations necessary to transform the primary experimental data. The measured pH values are corrected for any deviation from Nernstian slope of the glass electrode, for any change in the temperature from 298.16 K, and for the liquid-junction potential (for details see previous paper[33] in this series[35,36]).

The subroutine UBBEDC calculates the absorbance for each pH value [equation (2)] and a set of values of the parameters resulting at the particular stage of the minimization process. Subsequently, the sum U of the squares of the residuals is calculated [equation (5)]. The subroutine SKRDC gives as output the values of the parameters and their standard deviations, the statistical analysis of residuals and a graph of experimental and calculated points.

The other subroutines are basic in character and have been described in a previous contribution.[33] They are READI, READR, STATS, LETAG with internal subroutines MULLE, INVER, PINUS, and WEIGHT, PLOTT, SIMUL, NORAND and RANDOM.

A listing of the program DCLET, and instructions for preparation of input data and interpretation of output are available on request.

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SHORT COMMUNICATIONS

DCTA TITRATION OF IRON(III) WITH *p*-AMINOSALICYLIC ACID AND SODIUM AZIDE AS INDICATORS

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Summary—Iron(III) has been determined by DCTA titration with *p*-aminosalicylic acid and sodium azide as indicator at pH 1.4–3.5. The titrations are rapid, simple, accurate and reversible and as little as 0.15 mg of iron(III) can be determined in the presence of up to 100 times as much of certain ions. Cadmium, zinc, lead, copper(II), aluminium, thorium, oxalate, phosphate, fluoride and sulphide interfere. The method is utilized for determination of iron(III) in presence of copper(II) or lead and in limestone, cement and haemetite.

Since Přibil[1] proposed a direct titration of iron(III) with 1,2-diaminocyclohexanetetra-acetic acid (DCTA), various methods have been reported for its spectrophotometric[2] and visual[2–5] titration, but no attempt has been made to mask or remove interfering ions or to estimate iron in commercial or natural materials by these methods. In the present investigation, iron(III) has been determined alone and in the presence of various ions by direct titration with DCTA, *p*-aminosalicylic acid (PAS) and sodium azide being used as indicators, at pH 1.38–3.50 and 1.26–3.50 respectively. The work has been extended to determination of iron in mixtures with copper(II) or lead(II) and in limestone, cement and haemetite.

EXPERIMENTAL

Procedure

Iron(III) nitrate solution (0.005*M*, 0.5–5.0 ml) was diluted with water (20–25 ml) and titrated with DCTA solution of appropriate concentration after addition of 3 or 4 drops of 0.75% ethanolic PAS solution or 6 or 7 drops of 1.5% ethanolic sodium azide solution as indicator, at pH 1.38–3.50 and 1.26–3.50 respectively. The pH was adjusted either with sodium acetate and hydrochloric acid buffer (~5 ml) or by adding water and/or glacial acetic acid. The end-point was marked by a sharp colour change from violet red to light yellow with PAS and from orange red to greenish yellow with sodium azide. The titrations were also performed in the presence of various ions.

Potassium cyanide (~10 ml of 0.07% solution) was added before the buffer when copper(II) was present. The interference of lead was dealt with by adding ~1 ml of 0.5*M* sulphuric acid, neutralizing with ammonia and then buffering to the required pH.

Aluminium (up to 100 times the amount of iron) was masked by adding 5 ml of 0.5% sodium thiosulphate solution and 20 ml of water, then boiling free from sulphur dioxide and filtering. The filtrate was heated with a few drops of concentrated nitric acid, cooled, neutralized with ammonia, buffered and titrated.

Limestone, cement and haemetite were brought into solution by the usual methods, and fractions were titrated with DCTA by the procedure described, after removal of aluminium in the case of limestone and cement.

The titrations were repeated at least five times at each concentration level.

Table 1. Determination of iron(III) with DCTA

Metal ion added	Amount taken, *mg*		PAS indicator		Sodium azide indicator	
	Iron(III)	Metal ion	Iron(III) found, *mg*	Metal ion*† found, *mg*	Iron(III) found, *mg*	Metal ion*† found, *mg*
	0.15	—	0.15 (0.000)	—	0.15 (0.000)	—
	0.30	—	0.30 (0.000)	—	0.29 (0.002)	—
	1.35	—	1.34 (0.011)	—	1.36 (0.010)	—
Cu^{2+}	0.79	0.37	0.79 (0.000)	0.37 (0.000)	—	—
	0.89	0.73	0.90 (0.011)	0.74 (0.011)	—	—
	1.18	1.10	1.16 (0.010)	1.11 (0.013)	—	—
Pb^{2+}	1.04	1.04	1.04 (0.000)	1.04 (0.000)	1.04 (0.000)	1.04 (0.000)
	2.08	2.08	2.07 (0.011)	2.07 (0.013)	2.10 (0.013)	2.08 (0.000)
	8.32	3.12	8.28 (0.018)	3.13 (0.010)	8.35 (0.014)	3.11 (0.011)

* Standard deviation in brackets.
† From difference in titration values in presence and absence of masking agent.

RESULTS AND DISCUSSION

PAS alone has not previously been used as indicator for complexometric titration of iron(III), though a mixture of PAS and *p*-anisidine has been used for the EDTA titration of iron(III).[7] This mixture does not work satisfactorily with DCTA, but PAS alone is found to be excellent. The end-point with both PAS and azide is sharp and the titrations are simple, quick, reversible, quantitative, and satisfactorily carried out in the temperature range 25–60°. As little as 0.15 mg of iron(III) is determined quantitatively in 25 ml of solution in presence of 100 times as much lithium, sodium, potassium, ammonium, barium, calcium, strontium, magnesium, mercury(II), lanthanum, chloride, nitrate, acetate and sulphate ions. The titration is very slow in the presence of lanthanum at room temperature but fairly fast at 50–60°. The titration is not affected by silver ions or a precipitate of silver chloride. The end-point can be accurately detected in presence of chromium(III) chloride up to 0.4 and 0.2 mg/ml with PAS and sodium azide respectively. The end-point cannot be correctly detected in the presence of coloured compounds such as cobalt and nickel salts. Phosphate, fluoride and oxalate, which form stable complexes with iron(III), and sulphide (which reduces it), cause interference at all levels. Zinc does not interfere in the pH range 1.35–1.57 if PAS is used as indicator, but otherwise zinc, cadmium, lead, copper(II) and thorium interfere at all levels, being quantitatively co-titrated. Aluminium also interferes.

When PAS is used as indicator, copper can be masked by adding potassium cyanide solution, but sodium azide does not give any colour in the presence of cyanide ions. Lead is masked by precipitation of its sulphate. Aluminium is hydrolysed by boiling with sodium thiosulphate:

$$2Al^{3+} + 3S_2O_3^{2-} + 3H_2O \rightarrow 2Al(OH)_3 + 3SO_2 + 3S.$$

The iron(III) is reduced to iron(II) which is reoxidized with concentrated nitric acid after removal of the excess of thiosulphate, which otherwise interferes.

Table 2. Determination of iron(III) in certain substances

Substance	Iron found, *mg/g*		
	Official method	PAS	Sodium azide
Haemetite	610	608	609
	610	610	609
	607	607	608
Limestone	44.6	44.7	44.6
	44.6	44.6	44.7
	44.6	44.6	44.6
Cement	18.14	18.16	18.17
	18.15	18.12	18.18
	18.14	18.18	18.11

Aluminium in limestone and cement is removed before the iron is titrated. Other constituents of limestone, cement and haemetite do not interfere. The error does not exceed 0.2%.

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PHTHALANILIC ACIDS AS HIGHLY SELECTIVE REAGENTS FOR THE AMPEROMETRIC DETERMINATION OF THORIUM(IV)

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Summary—Th(IV) has been determined by amperometric titration at an applied emf of −1.0 V with ten phthalanilic acids. Of these, the 2,5-dichloro, 4-bromo, 3-nitro, 4-nitro and 1-naphthyl derivatives were found promising analytical reagents and most effective. Th(IV) in the range 11.6–1160 mg/100 ml can be determined with an error of ±0.3%. The possible interference of 46 ions was studied and only two, Pd(II) and Zr interfered; they could be masked by the addition of dimethylglyoxime or Nioxime, and pyrophosphate respectively.

In continuation of our previous work[1] on the amperometric determination of Th(IV), the reaction of phthalanilic acids with this metal ion was found to give promising results. The use of phthalanilic acid (**I**) and its p-tolyl (**II**), 2-methoxy (**III**), 4-fluoro (**IV**), 2-chloro (**V**), 2,5-dichloro (**VI**), 4-bromo (**VII**), 3-nitro (**VIII**), 4-nitro (**IX**) and 1-naphthyl (**X**) derivatives for the amperometric determination of thorium(IV) is described in this paper. These reagents are not only comparable to diphenic acid[1] but have the additional advantages of simpler preparation and practically no interference.

EXPERIMENTAL

Apparatus

As described earlier.[1]

Reagents and solutions

Thorium nitrate, sodium acetate, acetic acid and methanol were all of analytical grade. The phenylanilic acids were prepared by treating aromatic amines with phthalic anhydride in benzene at room temperature[2,3] and were crystallized from ethanol. The phenylanilic acid solutions were prepared in methanol, the other solutions were made in distilled water.

Procedure

A measured volume of standard substituted phenylanilic acid solution was taken in a 100-ml standard flask, 50 ml of acetate buffer (pH 3.5) were added and the solution was diluted to the mark with distilled water. An aliquot (10 or 20 ml) of this solution was transferred to a polarographic cell and deaerated by passage of pure nitrogen. An emf of −1.0 V (*vs.* SCE) was applied, with the dme as indicator electrode. This potential was found to give sharp end-points and to eliminate interferences. Measured volumes of standard thorium nitrate solution were added, then stirred in by passage of nitrogen, and the change in diffusion current was noted. The current was plotted against volume of titrant added, to locate the end-point (which occurs at an acid:thorium ratio of 1:1 as expected). The current decreases during the titration, and becomes constant beyond the end-point; in reverse titrations (thorium titrated with substituted acid) it is best to use an applied potential of −1.5 V. The current should first rise and then become constant after the end-point. Representative results for both titrations are presented in Table 1. The anilic acids from **VI** to **X** were found promising as analytical reagents for the amperometric determination of Th(IV).

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DISCUSSION

Effect of pH

The most accurate results were obtained in the pH range 2.7–4.6, maintained by the addition of sodium acetate–acetic acid buffer, which also serve as supporting electrolyte.

Thorium range

For titration with an error not exceeding 0.3%, the amounts of thorium per 100 ml of sample solution are 23–1160 mg for acids **I** and **II**, 15–580 mg for acids **III**–**V**, and 12–1160 mg for the others. Outside these limits the method is less accurate and the end-points are not very sharp.

Table 1. Amperometric determination of thorium(IV) with phthalanilic acids

Th(IV) present, *mg*	Th(IV) found, *mg*	Th(IV) present*, *mg*	Th(IV) found*, *mg*
500	501.5	450	450.9
400	398.8	350	351.1
300	299.1	250	250.7
200	200.5	150	149.6

* Reverse titrations.

Table 2. Determination of thorium in monazite (thorium present* = 6.49%)

Thorium found (A), %	Thorium found (B), %
6.47	6.65
6.48	6.64
6.51	6.63
6.50	6.60

* Thoron as colorimetric reagent.[4]
A Amperometric method.
B EDTA method using Xylenol Orange as indicator.

Determination of thorium in monazite

The method reported earlier[1] was used. The results were compared with those obtained complexometrically with Xylenol Orange as indicator (Table 2).

Interference studies

Interferences were studied by titration (direct and reverse) of reagent solution with thorium nitrate solution containing a 5–10-fold amount of the foreign ion. NH_4^+, K^+, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, VO^{2+}, UO_2^{2+}, Fe^{3+}, Al^{3+}, As^{3+}, Cr^{3+}, Sb^{3+}, Bi^{3+}, Ce^{3+}, La^{3+}, In^{3+}, Ga^{3+}, Y^{3+}, Rh^{3+}, Nd^{3+}, Ce^{4+}, Ti^{4+}, Sn^{4+}, NO_2^-, Cl^-, Br^-, I^-, CNS^-, SO_4^{2-}, CO_3^{2-}, $C_2O_4^{2-}$, SO_3^{2-}, $S_2O_3^{2-}$, PO_4^{3-}, $P_2O_7^{4-}$, citrate and tartrate ions do not interfere. The interference due to Pd^{2+} can be removed by the addition of dimethylglyoxime or Nioxime, and that due to Zr^{4+} by addition of pyrophosphate.

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DETERMINATION OF ANTIMONY(III) WITH POTASSIUM HEXACYANOFERRATE(III)

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Summary—The determination of antimony(III) with potassium hexacyanoferrate(III) in 5*M* hydrochloric acid medium and in the presence of 40% v/v acetic acid is described. Ferroin is used as the indicator. Antimony has been determined in tartar emetic, solder and pig lead. Arsenic(III) does not interfere.

No convenient procedure for the direct titration of antimony(III) with potassium hexacyanoferrate(III) has been described to date. Fresno and Valdes[1] performed the titration potentiometrically at 50–70° in concentrated sodium hydroxide solution, and Kiboku[2] carried it out indirectly by precipitating antimony(III) as sulphide, redissolving it in sodium hydroxide or sodium carbonate solution, and titrating the sulphide ions with hexacyanoferrate(III), using sodium nitroprusside as indicator. Zhdanov and Kuruchkina[3] studied the amperometric titration and concluded that erroneous and unreproducible results are obtained. In this communication we report a simple procedure for the direct titration of antimony(III) with potassium hexacyanoferrate(III), using ferroin as indicator. The procedure has been applied to the determination of antimony in tartar emetic, pig lead and solder.

EXPERIMENTAL

Reagents

Antimony(III) solution, 0.05M. Dissolve antimony(III) chloride in 3*M* hydrochloric acid.

Potassium hexacyanoferrate(III), 0.1M.

Tartar emetic solution, 0.05M.

Ferroin solution, 0.025M.

All the other reagents used were made with analytical-reagent grade chemicals. The standard solutions were standardized titrimetrically.[4,5]

Procedure

Treat a suitable volume of the antimony(III) solution with enough concentrated hydrochloric and glacial acetic acid to make their concentrations 5*M* and 40% v/v respectively. Dilute to 100 ml and titrate with a standard potassium hexacyanoferrate(III) solution, using a drop of ferroin solution as indicator.

Antimony in pig lead and solder

Weigh accurately about 1 g of sample into a beaker, add 10 ml of concentrated sulphuric acid, cover and heat until the alloy has been decomposed. Decant the clear liquid from the lead sulphate into a conical flask and boil for 5 min to expel sulphur dioxide. Boil the residue with 40 ml of 6*M* hydrochloric acid until the lead sulphate dissolves completely and add to the main antimony solution, disregarding any lead salt which may reprecipitate. Add 50 ml of glacial acetic acid and one drop of ferroin solution and titrate with standard potassium hexacyanoferrate(III) as described above.

RESULTS AND DISCUSSION

Because the electrode potentials are very sensitive to the solvent and acidity the potentials of the ferricyanide/ferrocyanide and antimony(V)/antimony(III) couples have been determined for a range of acid con-

Table 1. Potentials of the ferricyanide/ferrocyanide and antimony(V)/antimony(III) couples

In 40% v/v acetic acid			In 5*M* hydrochloric acid		
	Potential *vs.* NHE, *V*			Potential *vs.* NHE, *V*	
[HCl], *M*	$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	Sb(V)/Sb(III)	$[CH_3COOH]$,% *v/v*	$Fe(CN_6^{3-}/Fe(CN)_6^{4-}$	Sb(V)/Sb(III)
1	0.850	0.861	0	0.982	0.890
2	0.955	0.855	10	1.027	0.868
3	1.041	0.834	20	1.101	0.850
4	1.121	0.808	30	1.134	0.818
5	1.135	0.786	40	1.138	0.786
6	1.138	0.772			

Table 2. Determination of antimony with hexacyanoferrate(III)

Sb(III) taken, *mg*	Sb(III) found, *mg*
9.29	9.31
21.2	21.3
30.0	30.0
38.4	38.5
50.3	50.6
55.8	55.9

Table 3. Determination of antimony in pig lead and solder

Sample	Sample, *g*	Antimony found, %: Hexacyanoferrate(III)	Antimony found, %: Potassium bromate
Pig lead	1.0240	4.78	4.78
	1.2014	4.80	4.81
	1.4888	4.76	4.76
	1.6206	4.75	4.80
	1.9898	4.78	4.80
Solder	1.0122	4.67	4.68
	1.3864	4.69	4.65
	1.5920	4.70	4.70
	1.8046	4.67	4.68
	2.0082	4.72	4.70

centrations and solvent mixtures. Potentials were determined with a bright platinum rod as indicator electrode and a saturated calomel electrode as reference, with a saturated KCl salt bridge. The results are shown in Table 1.

From the data presented above, it is clear that the potential of the ferricyanide/ferrocyanide couple increases with increasing acid concentration whereas that of the antimony(V)/antimony(III) couple decreases.

Although the difference in the potentials of the two systems in 4*M* hydrochloric acid/40% v/v acetic acid seems sufficiently large (0.313 mV) for potentiometric titration to be successful, the reaction is slow near the end-point, the potential taking 5–10 min to stabilize, although at the start of the titration it stabilizes rapidly. However, successful titrations are possible at hydrochloric acid concentrations of 5*M* or greater in 40% v/v acetic acid. The end-point may be detected visually, with ferroin as indicator, or potentiometrically. The potentials stabilize within 1 min and a potential jump of 150–180 mV/0.04 ml is obtained.

In view of the criticality of the concentration it must be stressed that in the procedure for preparation of the solution for titration, the acidity refers to the starting solution. With an aliquot of more than 10 ml of 0.1*N* antimony(III) the initial volume must exceed 100 ml, because a turbidity or precipitate (possibly of ferrocyanic acid[6]) occurs if the antimony concentration exceeds 0.6 g/l. An indicator blank is needed if 0.01*N* solutions are used. Typical results are shown in Table 2.

Interferences

Arsenic(III), manganese(II), aluminium, nickel, zinc, lead, borate, tartrate, citrate, oxalate, phosphate and sulphate do not interfere, but iron(II), sulphide, sulphite and thiosulphate do.

Test determinations

Antimony has been determined in tartar emetic under the conditions described above. The results obtained agreed closely with those obtained by the bromate method.[4] Results for antimony in lead and solder are given in Table 3.

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MEILLEURE EVALUATION DU CARBONATE PAR DOSAGE PROTOMETRIQUE EN SYSTEME FERME

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Résumé—L'impureté carbonate perturbe fréquemment les dosages protométriques. Pour tenir compte rigoureusement de l'équilibre liquide–gaz [$H_2CO_3 \rightleftharpoons CO_{2(g)} + H_2O$] un nouveau mode opératoire, qui consiste à effectuer les neutralisations en système fermé avec un certain volume de phase gaz, est proposé. Les équations correspondantes, exploitées par affinement multiparamétrique, sont appliquées avec succès au cas extrême de la neutralisation d'un acide fort par une solution de carbonate de sodium.

Dans un travail antérieur relatif à la détermination de constantes d'acidité par affinement multiparamétrique[1] nous nous sommes heurtés au problème de la prise en compte de l'impureté carbonate introduite par la base forte titrante. Les neutralisations correspondantes, effectuées sous courant d'azote, ne peuvent donner lieu qu'à des traitements mathématiques approchés car le dégagement de gaz carbonique est variable.

Devant l'imperfection des calculs appliqués à ces systèmes ouverts nous avons pensé imposer la conservation des masses en travaillant en système fermé. Les équations tiennent alors compte d'un équilibre liquide-gaz [$H_2CO_3 \rightleftharpoons H_2O + CO_{2(g)}$] et ont été établies dans le cas général des mélanges de protolytes.[1] La nouvelle technique de neutralisation consiste simplement à travailler en cellule fermée, avec un certain volume de phase gaz. Nous décrivons dans cet article le cas extrême, par la prédominance de l'équilibre liquide-gaz, de la neutralisation d'un acide fort par le carbonate de sodium. Si ce procédé se révèle valide, il sera encore plus aisé d'application lorsque le carbonate n'est qu'une impureté.

RAPPEL D'ELEMENTS THEORIQUES

Dans le cas de la neutralisation d'un acide fort par le carbonate de sodium, l'expression générale du volume de réactif v_e se réduit[1] à

$$v_e = v_0 \frac{H_i^0 - h + K_w/h}{C_s^0\left(\frac{2(1+G)\beta_2 h^2 + \beta_1 h}{(1+G)\beta_2 h^2 + \beta_1 h + 1}\right) + h - K_w/h}$$

où

$$G = (v_g - v)/(v_0 + v)RTK_p$$

v_0, v_g, v = volumes initiaux de la solution et de la phase gaz, volume de réactif expérimental

β_1, β_2 = constantes globales de formation de HCO_3^- et H_2CO_3

K_p = constante d'équilibre = $[H_2CO_3]/p_{CO_2}$

H_i^0, C_s^0 = concentrations initiales en acide fort et en carbonate.

h = concentration en H^+

Rigoureusement, il faudrait introduire v_e dans l'expression de G ce qui conduirait à résoudre une équation du second degré en v_e ou à mener un calcul itératif. Cependant le volume expérimental v est maintenu dans l'expression de G. Cette approximation est licite lorsque v est nettement inférieur à v_0 et v_g, que les résidus $(v - v_e)$ sont faibles ou que le carbonate devient une impureté. Il a été vérifié dans le cadre de l'exemple suivant que cette approximation conduisait aux mêmes résultats que le traitement rigoureux.

PARTIE EXPERIMENTALE

La neutralisation de 100 ml (v_0) d'acide chlorhydrique ($5.10^{-4}M$) par le carbonate de sodium ($5.10^{-2}M$) est effectuée dans un vase thermostaté à 25° et à une force ionique de 0,1M en nitrate de potassium. On prend simplement soin de rendre hermétique la cellule de titrage "Tacussel RM 06" par graissage des différents rodages. Avec un tel volume de solution initiale et en tenant compte du volume occupé par les électrodes et la pointe de seringue, le volume de la phase gaz (v_g) est de 190,0 ± 0,5 ml.

Le réactif est ajouté par une seringue micrométrique "Gilmont" de 2,5 ml ayant une résolution de 10^{-4} ml. La valeur du potentiel (potentiomètre "PHM 64 Radiometer") est notée lorsque la dérive est inférieure ou égale à 0,1 mV/mn. Dans ces conditions la manipulation dure environ 8 hr, les équilibres se stabilisant lentement dans la région tampon intermédiaire (Fig. 1a; $0,5 < v < 1$ ml) où se produit la redissolution du $CO_{2(g)}$ formé en milieu acide.

Il a été vérifié dans une autre manipulation que la pente des électrodes (verre "Schott, type U", référence au calomel) est nernstienne. Le calcul du décalage d'origine ϵ

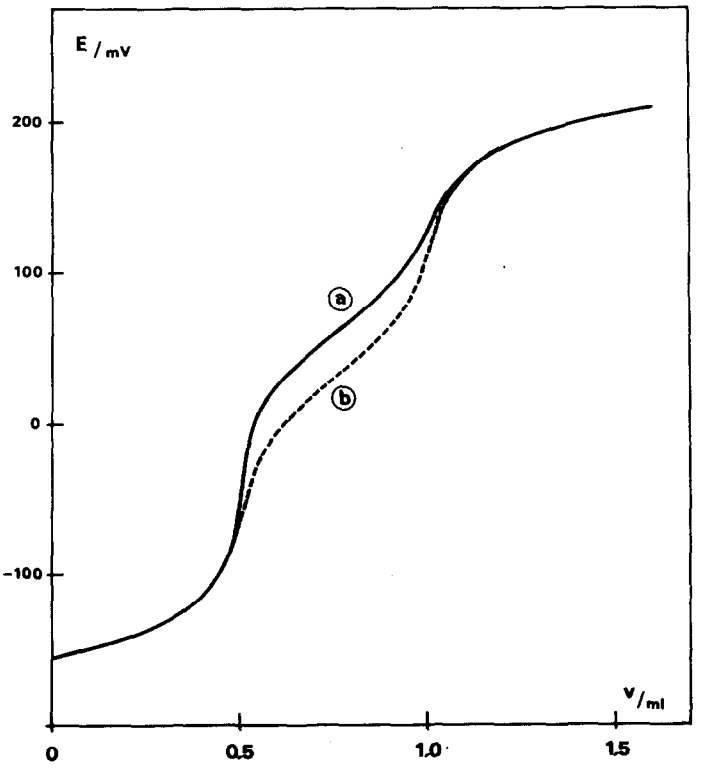

Fig. 1. Neutralisations d'un acide fort par le carbonate de sodium en milieu fermé ($H_i^0 = 5.10^{-4}M$; $v_0 = 100$ ml); (a) $v_g = 190$ ml; (b) allure de la courbe pour $(v_g - v) = 0$

($\epsilon = E^*/0{,}05916s + \log \gamma$, avec E^*: potentiel normal, s: sensibilité de l'électrode de verre, γ: coefficient d'activité)[3] de cette chaîne de mesure, assimilable à un potentiel normal, est conjoint à celui des autres paramètres.

RESULTATS

L'affinement des paramètres inconnus est mené, à l'aide du programme MUPROT,[1] en minimisant

$$S = \Sigma(v - v_c)^2 \Big/ \left[\sigma_{0v}^2 + \sigma_{0E}^2\left(\frac{\partial v}{\partial E}\right)^2\right] \text{ où } \sigma_{0v}^2 \text{ et } \sigma_{0E}^2$$

sont les variances sur v et E. Le choix de σ_{0v} et σ_{0E}, habituellement basé sur les résolutions de l'appareillage, est ici plus délicat. En effet, la valeur de σ_{0E} est inconnue car à la résolution du potentiomètre viennent s'ajouter les défauts d'équilibre. En nous basant sur l'écart-type final, qui doit être proche de l'unité, nous avons pu remonter à une valeur acceptable ($\sigma_{0E} = 1$ mV). Cependant, il est manifeste que σ_{0E} n'est pas constant: il faudrait logiquement introduire une variance qui dépend du temps de mise en équilibre; nous délaisserons pour l'instant cet aspect du problème qui sort du cadre de cette communication.

Avec les données d'une seule manipulation il nous a été impossible de calculer simultanément K_p et β_2 qui sont fortement corrélés: la variation du volume de la phase gaz est trop faible pour pouvoir distinguer correctement ces deux paramètres. Pour lever l'indétermination, il faut disposer de la valeur de K_p ou d'au moins une manipulation effectuée avec un v_g différent. L'exploitation, dans les mêmes conditions de pondération, des données obtenues antérieurement en travaillant sous huile de vaseline[2,3] donc avec $(v_g - v) = 0$, donne $\log \beta_1 = 9{,}75$; $\log \beta_2 = 15{,}89$.

Le tableau suivant comporte les résultats obtenus en maintenant dans l'affinement la différence ($\log \beta_2 - \log \beta_1 = 6{,}14$) ou en fixant K_p à la valeur de la littérature[4]; ceux-ci sont cohérents vu les domaines de confiance. L'identité des écarts-types indique que l'on peut s'accorder une légère incertitude sur le couple (β_2, K_p) sans fausser l'ajustement.

Le terme $(v_g - v)/(v_0 + v)$ varie de 1,900 à 1,854 durant la neutralisation: à la limite il peut être considéré comme constant, compte tenu des autres erreurs expérimentales. Cette approximation entraîne le changement de variable suivant:

$$\left(1 + \frac{v_g - v}{(v_0 + v)RTK_p}\right)\beta_2 \sim \beta_2^* = \text{constante}$$

Mais le paramètre β_2^* ainsi calculé (voir tableau 1) n'est utilisable que si les caractéristiques géométriques de la cellule et le volume v_0 sont maintenus pour les manipulations ultérieures.

Dans tous les cas, la concentration en carbonate C_x^0 est correctement retrouvée.

Remarquons que pour une composition donnée de

Tableau 1. Résultats des ajustements multiparamétriques*

Paramètres	β_2 fixé	K_p fixé	Changement de variable $\beta_2^* = f(K_p, \beta_2)$
log β_1 (3σ)	9,76 (0,03)	9,76 (0,03)	9,76 (0,03)
log β_2 (3σ)	15,90	15,86 (0,05)	log β_2^* = 16,37 (0,05)
log K_p (3σ)	−1,40 (0,07)	−1,47	
C_v^0 (3σ), M	4,98 (0,02).10^{-2}	4,98 (0,02).10^{-2}	4,98 (0,02).10^{-2}
décalage d'origine ϵ (3σ)	5,915 (0,002)	5,915 (0,002)	5,915 (0,002)
Ecart-type	1,14	1,14	1,15

* 35 points expérimentaux. $\sigma_{0v} = 10^{-4}$ ml; $\sigma_{0E} = 10^{-3}$ V. Paramètres fixés: $H_i^0 = 5.10^{-4}M$; $K_w = 1{,}40.10^{-14}$; pente des électrodes = 1/0,05916.

la solution ($NaHCO_3$, $CaCO_3$...) et avec du CO_2 provenant de l'extérieur, le système que nous venons de décrire est très proche des premiers procédés utilisés pour la détermination du p_{CO_2} des gaz, par la mesure du pH.[5–7]

Les valeurs de β_1, β_2, K_p ou β_2^* étant maintenant connues, il va être possible de tenir compte rigoureusement de l'impureté carbonate dans toute neutralisation, à l'aide de l'expression générale de v_c.[1] Cependant, cette technique de titrage en milieu fermé souffre de la lenteur de stabilisation de l'équilibre liquide–gaz, surtout dans le sens de la redissolution du CO_2 formé. Il faut néanmoins se souvenir que lorsque le carbonate est en faible concentration, seuls quelques relevés sont concernés par ce problème de stabilisation. De plus, nous pensons accélérer la mise en équilibre en utilisant une pompe péristaltique qui réinjectera en solution le CO_2 formé et en réduisant le volume de la phase gaz.

Bien qu'elle soit la plus avantageuse, la technique que nous venons d'exposer est inédite pour ce qui est des neutralisations suivies par potentiométrie. Tout autre équilibre liquide–gaz se traite de la même façon à condition que le gaz se comporte comme un protolyte (NH_3, SO_2, NO_2...). Ce type de procédé, qui est garant de la reproductibilité des résultats et qui se prête bien à l'automatisation, sera systématiquement utilisé dans l'avenir. Nous espérons qu'il se généralisera au détriment de la technique utilisant le passage d'un courant d'azote dans la solution. D'autres débouchés sont envisagés pour les équations introduites pour la prise en compte des équilibres liquide–gaz puisque le cas d'un protolyte extractible ou participant à un échange d'ions, se traite avec des expressions comparables. Une application intéressante de l'extraction liquide–liquide peut être alors envisagée dans le cas de l'analyse de mélanges. En effet, des protolytes d'acidité très proche peuvent présenter des extractibilités différentes: on observera alors un glissement de leurs propriétés acides, ce qui facilitera leur discrimination par pH-métrie (cas analogue à celui de la figure 1).

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Summary—Carbonate as impurity often interferes in acid–base titrations. To take into account the liquid–gas equilibrium [$H_2CO_3 \rightleftharpoons CO_{2(g)} + H_2O$)] a new method is proposed: neutralizations are performed in a closed system with a known volume of gaseous phase. The corresponding equations, processed by multiparametric refinement, are successfully applied in the extreme case, *viz.* neutralization of a strong acid by sodium carbonate solution.

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ZERO-CURRENT BIPOTENTIOMETRIC END-POINT INDICATION WITH PRETREATED ELECTRODES—V*

USE OF PRETREATED TIN OXIDE ELECTRODES

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Summary—The redox response of a tin oxide electrode is determined. A pair of differently pretreated tin oxide electrodes is used for zero-current bipotentiometric indication of the end-point in redox titrations.

Thin-film tin oxide layers, generally deposited on glass, have recently been used as working electrodes in electrochemical investigations.[1] This is due to some favourable properties[2–10] such as mechanical and electrochemical stability (broad accessible potential range), low double-layer capacitance, lack of extensive surface reactions, and good optical transparence, allowing the spectrophotometric investigation of electrode reactions.[11] Their electrocatalytic activity can be strongly influenced by doping with electron donors or acceptors[1–10] or by chemical modification of the electrode surface.[12–14] Slight pretreatment effects have also been observed.[1,7] Tin oxide film electrodes were used as indicating electrodes in redox titrations by Cooper.[15] Further analytical uses reported are in coulometry[16–18] and stripping analysis.[19] Bulk tin oxide in the form of specially prepared pellets is used as an analytical sensor for combustible and toxic gases.[20,21] The present paper deals with the use of tin oxide film electrodes as a bipotentiometric indicator system. Of the many possibilities for obtaining a zero-current bipotentiometric signal,[22] that based on the use of two differently pretreated tin oxide electrodes is reported.

EXPERIMENTAL

The electrodes used consisted of small glass rods covered with tin oxide film doped with antimony, obtained by thermal decomposition of a tin(IV) chloride solution in alcoholic hydrochloric acid containing antimony(III) chloride. The rods were fixed at one end in a plastic tube, electrical contact being ensured by pressing a thin copper ring onto the film surface. Bipotentiometric titrations were performed as described earlier.[23] One of the electrodes was untreated, the pretreatments applied to the other were: (*a*) soaking with conc. nitric acid for 50 sec; (*b*) soaking with 1% potassium iodide solution for 1 min; (*c*) soaking with 0.5*M* iron(II) sulphate in 2*N* sulphuric acid for 1 min. Two kinds of redox titrations were performed: chemically reversible (Fe^{2+} with Ce^{4+}), and irreversible (Fe^{2+} with $Cr_2O_7^{2-}$ or MnO_4^-). For comparison the titrations were done with end-point indication by a pair of platinum electrodes prepared in the same way as the tin oxide electrodes.

RESULTS

In order to select the best pretreatment combinations, the effect of a given pretreatment on the redox sensitivity of tin oxide electrodes was tested by observing the redox potential exhibited in a mixture of 0.1*M* potassium ferricyanide and 0.1*M* potassium ferrocyanide in different ratios as indicated in Fig. 1. Constant ionic strength was provided by potassium chloride. It can be seen that regardless of the pretreatment used, the electrode response is linear over a range of [ox]/[red] ratios from 100 to 0.1. The untreated electrode has a slightly broader linearity range (ratios 100–0.01). At extreme [ox]/[red] ratios, deviations from linearity appear, which depend on the pretreatment used. Platinum electrodes showed very similar behaviour, including the pretreatment effect. The response of the tin oxide electrode in the redox system investigated, calculated by the least-squares method, is

$$E = 442 + 52 \log[\text{Fe(III)}]/[\text{Fe(II)}], \text{ mV}$$

A Nernst slope of 52 mV/decade was also found for platinum. The response times also were identical.

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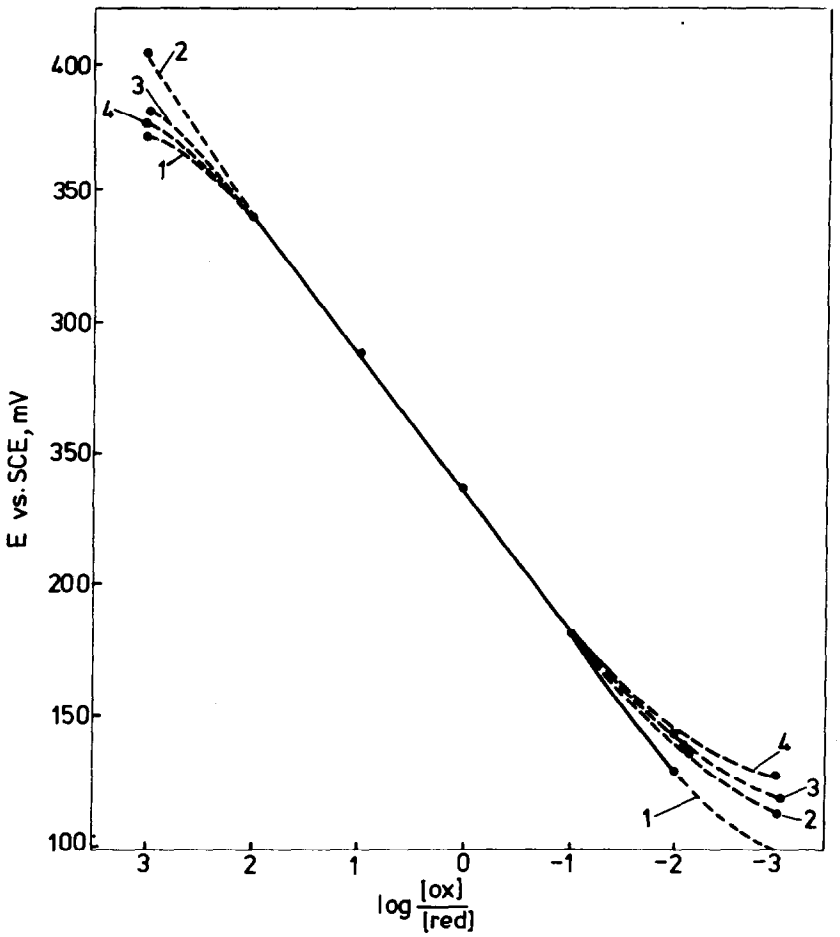

Fig. 1. Redox sensitivity of tin oxide electrodes in the $K_3Fe(CN)_6/K_4Fe(CN)_6$ system. Pretreatments applied: 1—untreated; 2—soaked with conc. HNO_3; 3—soaked with $FeSO_4$; 4—soaked with KI. $f = [K_3Fe(CN)_6]/[K_4Fe(CN)_6]$.

The potentiometric titration curves for Fe^{2+} with Ce^{4+} are nearly identical both with tin oxide and platinum electrodes, characterized by a large potential jump of 500–600 mV at the equivalence point. In the case of the irreversible titration system (Fe^{2+} with $Cr_2O_7^{2-}$ or MnO_4^-) the potential jump observed with the tin oxide electrode was approximately 100 mV smaller than that observed with the platinum electrode.

The zero-current bipotentiometric equivalence signal obtained with the tin oxide electrode pair in both titration systems investigated was considerably sharper than that obtained with the platinum electrodes (Figs. 2 and 3). The equivalence volumes indicated by the peak of the signal correspond to the theoretical values within the usual titration error limits. Reproducibility was ensured by renewal of the pretreatments before each titration. The standard deviations (ml) of ten bipotentiometric titrations (tin oxide electrodes) were: 0.017 (Fe^{2+} with Ce^{4+}), 0.166 (Fe^{2+} with $Cr_2O_7^{2-}$), and 0.182 (Fe^{2+} with MnO_4^-) respectively. In conclusion: tin oxide electrodes have similar redox behaviour to platinum and exhibit the same pretreatment effects; thus they are suitable for use as working electrodes in zero-current bipotentiometric redox titrations.

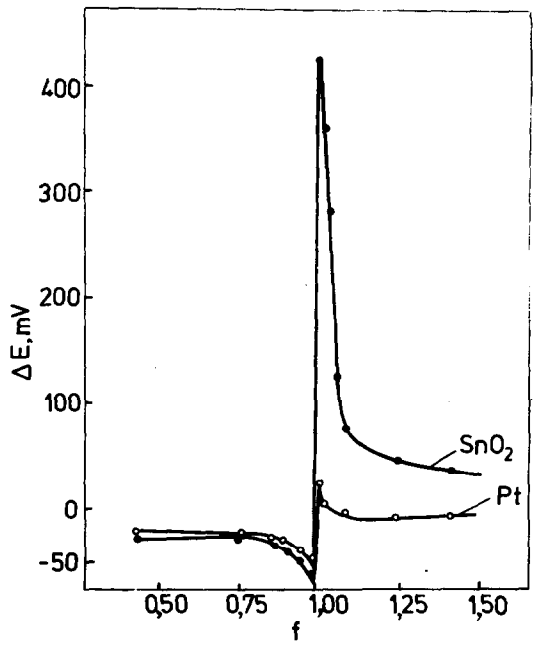

Fig. 2. Zero-current bipotentiometric titration curves of 10 ml of 0.01*M* Fe^{2+} with 0.1*M* Ce^{4+}. ΔE—potential difference between the two working electrodes; f—degree of titration.

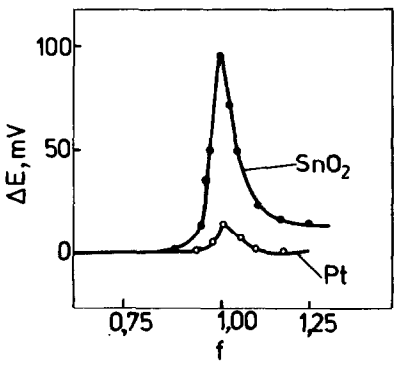

Fig. 3. Zero-current bipotentiometric titration curves of 10 ml of 0.01*M* Fe^{2+} with 0.05*M* $Cr_2O_7^{2-}$. ΔE—potential difference between the two working electrodes; *f*—degree of titration.

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THE USE OF BRILLIANT GREEN IN ION-PAIR CHROMATOGRAPHY

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Summary—Brilliant Green is used as the stationary phase in the ion-pair chromatography of butanoic, pentanoic, octanoic and lauric acids, with hexane–dichloromethane as eluent.

Ion-pair chromatography is a useful technique for separating ionizable compounds. Since its introduction by Eksborg and Schill[1] the technique has been used quite extensively and many applications of ion-pair chromatography have been reported in the literature.[2–7]

The most popular mode of ion-pair chromatography involves separation in a reversed-phase system[8–10] on a chemically bonded ODS column. In this type of system the ion-pairing counter-ion is present in the polar mobile phase. Although the mechanism is in dispute,[11] the process can be adequately described as ion-pair formation occurring in the mobile phase with the hydrophobic ion-pairs partitioning into the non-polar stationary phase.

Another approach to ion-pair chromatography involves a normal-phase system in which the ion-pairing counter-ion is present in the polar stationary phase.[12,13] This technique has not been used extensively, because the reversed-phase technique is more convenient. In the normal-phase technique, careful equilibration of the mobile and stationary phases, temperature control and the use of a presaturation column are usually necessary if good results are to be obtained. Also, when compared with the reversed-phase technique, normal-phase ion-pair chromatography suffers from low efficiency, peak asymmetry and low sample capacity.[9]

Normal-phase ion-pair chromatography offers one advantage over the reversed-phase technique. By proper selection of the ion-pairing counter-ion, the normal-phase system can be used for the separation and detection of trace levels of ionizable solutes which cannot be detected with a photometric detector. In normal-phase ion-pair chromatography the ionic solute will exist as an ion-pair in the non-polar mobile phase. By selection of a counter-ion which exhibits a strong absorbance, and monitoring the absorbance with a photometric detector, a convenient system can be developed for the detection of non-absorbing solutes at levels below the detection limit of a refractive index detector (around 10 μg under ideal conditions[14,15]). This principle was first introduced by Eksborg *et al.*[16]

Lagerstrom[6] and Eksborg *et al.*[16] used a quaternized tricyclic antidepressant, *N*,*N*-dimethylprotriptyline ($\epsilon = 4 \times 10^3$ l.mole^{-1}.cm^{-1}, $\lambda = 254$ nm), to separate three carboxylic acids of widely different molecular weight. Using this as the counter-ion in their normal-phase system, they separated and detected 0.16 μg of benzilic acid, 0.18 μg of phenylbutyric acid and 0.19 μg of salicylic acid. They estimated that the detection limit would be at least one order of magnitude lower.

Cationic (and anionic) dyes possess properties which are well suited for use as counter-ions in normal-phase ion-pair chromatography. These compounds generally exhibit strong absorbance in the visible spectrum, which should permit very low detection limits for non-absorbing ionizable solutes. This paper describes the use of a triphenylmethane dye as the counter-ion in normal-phase ion-pair partition chromatography of a series of short-chain aliphatic acids used as a model series of solutes. Several triphenylmethane dyes were examined, including Brilliant Green, Crystal Violet and Malachite Green. In preliminary batch extractions, only Brilliant Green ($\epsilon = 8.8 \times 10^4$ l.mole^{-1}.cm^{-1}, $\lambda_{max} = 630$ nm) formed extractable species with the fatty acid anions and it was, therefore, chosen for the work described here.

EXPERIMENTAL

Apparatus

A Model 3500B Spectra-Physics Liquid Chromatograph coupled with a Schoeffel SF770 Spectroflow variable-wavelength detector was used for all separations. Data were analysed with an Autolab System I Computing Integrator (Spectra-Physics). Absorbance measurements were made with a Cary 14 spectrophotometer.

Reagents

Brilliant Green (Eastman), dye content 94–97%, was used as received. Further purification was found unnecessary since it did not affect the amount of dye extracted

into the organic phase. All other chemicals used were reagent grade. Demineralized water was used in the initial extraction studies.

Chromasorb P 60–80 mesh, acid-washed (Johns-Manville), Porasil B/250, 37–75 μm (Waters Associates), and Corning Uncoated Controlled Pore Glass 75–125 μm and 5–10 μm (Pierce Chemical Co.) were used as stationary-phase support materials.

Chromasorb P 125–150 μm, was obtained by grinding and sieving Chromasorb P 60–80 mesh.

Procedure

Columns were packed either by the balanced-density slurry or dry-packing techniques, depending on particle size. All support materials were oven-dried before use. For particles ≤ 10 μm in diameter the balanced-density slurry method[17] was used. The slurry was obtained by mixing 1.5–2.0 g of support material with 20 ml of a 1:1 v/v mixture of tetrabromoethane and butanol. The slurry was finally adjusted by observing the direction in which the particles tended to migrate after 30 min and adding the appropriate solvent to stop the migration. The column was packed by a method previously described.[18]

After packing with the support material, the columns were prepared by the *in situ* coating technique.[19] The columns were flushed with 50 ml of ethanol or methanol followed by approximately 30 ml of stationary phase. The excess stationary phase was removed by flushing the column with hexane. In general, this required about 200 ml of hexane.

The stationary phase consisted of aqueous solutions of Brilliant Green (0.01–0.05*M*) buffered to pH = 6.1 with 0.2*M* phosphate buffer. The stationary phase was filtered through a 0.45-μm filter before coating the column.

The samples were injected in either the acid form or as the ion-pair, dissolved in the mobile phase (a mixture of hexane and dichloromethane.

All experiments were performed at ambient temperature (22 ± 3°).

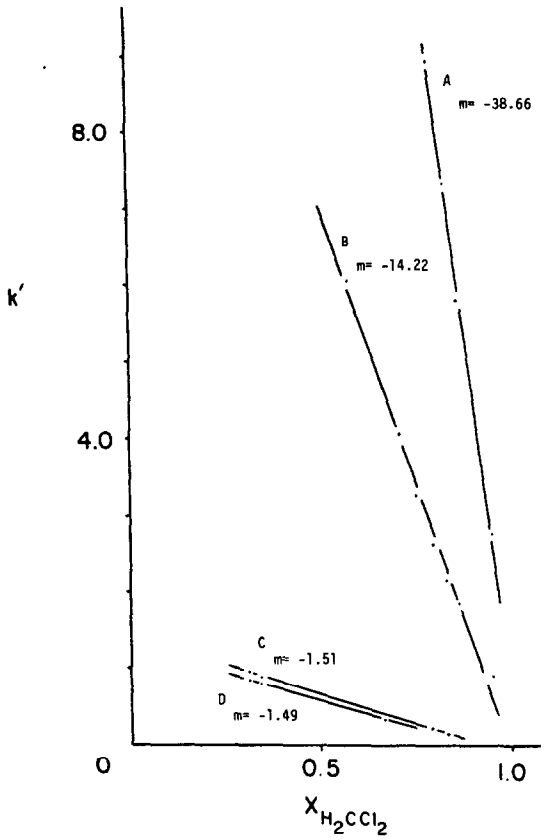

Fig. 2. Change in capacity factor with mobile phase composition: A, butanoic acid; B, pentanoic acid; C, octanoic acid; D, lauric acid. Stationary phase: 0.05*M* Brilliant Green, 0.2*M* phosphate buffer pH = 6.1, coated on 5–10 μm controlled pore glass.

RESULTS AND DISCUSSION

The composition of the mobile phase was found to be the most important factor in determining the overall chromatographic characteristics of the method. Figure 1 illustrates the influence of the mobile phase composition on both the resolution and sensitivity of the method. As the proportion of dichloromethane in the mobile phase increases, the peak area, and therefore sensitivity, increases. A change from 60% to 70% dichloromethane in the mobile phase increases the peak area by a factor of 4 for both octanoic and pentanoic acids. Under these conditions, however, the resolution[14] decreases. For the mobile phase containing 60% dichloromethane the resolution is calculated to be 1.31, while with the 70% mixture it decreases to 0.91.

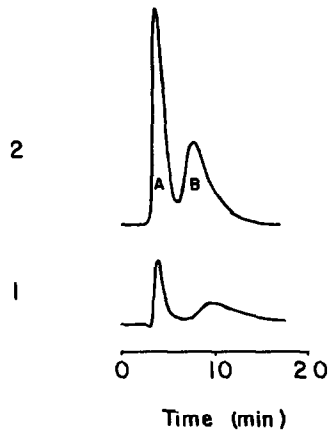

Fig. 1. Effect of mobile phase composition on sensitivity and resolution: A, octanoic acid; B, pentanoic acid. Mobile phase: 1, 60% H_2CCl_2/40% hexane; 2, 70% H_2CCl_2/30% hexane; stationary phase: 0.05*M* Brilliant Green, 0.2*M* phosphate pH = 6.1, coated on Chromasorb P, 60–80 mesh.

The effect of the mobile phase composition on the capacity factor for several short-chain fatty acids is shown in Fig. 2. The capacity factor is found to vary inversely with the mole fraction of dichloromethane in the mobile phase. A linear least-squares fit to the data gave the following: butanoic acid, $m = -38.66$, $r = 0.9969$; pentanoic acid, $m = -14.22$, $r = 0.9923$; octanoic acid; $m = -1.51$, $r = 0.9999$; lauric acid, $m = -1.49$, $r = 0.9997$.

From the data in Fig. 2 it is apparent that the chromatographic behaviour of the heavier acids is influenced to a lesser degree by changes in the mobile phase composition than that of the lighter acids. The heavier acids, being more hydrophobic than the

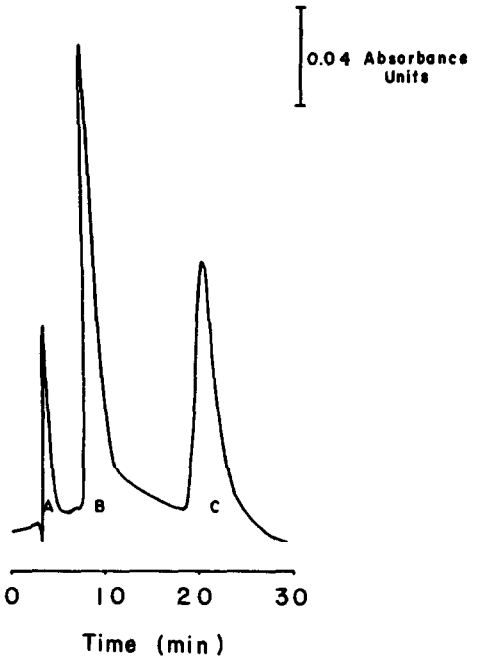

Fig. 3. Separation of octanoic, pentanoic, and butanoic acids: A, 14 μg of octanoic acid; B, 31 μg of pentanoic acid; C, 27 μg of butanoic acid. Mobile phase: 70% H_2CCl_2/30% hexane, flow-rate 0.6 ml/min. Stationary phase: 0.05*M* Brilliant Green, pH = 6.1, 0.2*M* phosphate buffer, coated on 75–125 μm controlled pore glass.

lighter acids, exhibit more favourable partitioning as ion-pairs into the organic solvent. This explains the elution order of the acids as indicated in Fig. 2. The heavier, more hydrophobic, acids are eluted before the lighter acids.

The data in Figure 2 indicate that it should be possible to separate the heavier fatty acid with the system described. As the amount of dichloromethane in the mobile phase decreases, the difference in the capacity factor for lauric and octanoic acids increases. With a mobile phase composition of 18% dichloromethane and 82% hexane the capacity factor for octanoic acid is 0.94 and for lauric acid 0.85. To separate the acids under these conditions would require a column 110 cm long.

Figure 3 shows the separation of three low molecular-weight fatty acids. The separation was achieved by isocratic elution with 70% dichloromethane, 30% hexane. The data show that Brilliant Green can be used to separate the short-chain fatty acids. The dye counter-ion offers enough selectivity to allow the separation of acids differing by only one methyl group, with a high degree of sensitivity. Amounts as small as 20 ng have been detected.

Three materials were tested for use as supports for the aqueous stationary phase: Chromasorb P, Porasil/B/250, and Corning Uncoated Controlled Pore Glass. Both Chromasorb P and Controlled Pore Glass were found to be compatible with the stationary phase used. Porasil/B/250 was found to be unacceptable as a support material. Porasil is a highly active silica support and tended to adsorb the dye counter-ion very strongly. This interfered with ion-pair formation and no signal was observed when this support material was used. The best sensitivity was obtained when Chromasorb P was used as the stationary phase support.

The major problem associated with the method described is the relatively short column lifetime. In general, the column has a useful lifetime of 20–30 hr. The tendency of the triphenylmethane dyes to form neutral carbinols[20] is the most important factor in determining column lifetime. The formation of the carbinol tends to increase losses of dye from the column by increasing dye solubility in the mobile phase. For this reason, equilibrated mobile phases did not play a major role in determining column lifetime, since their use did not increase it significantly. Fortunately, the rate of carbinol formation from Brilliant Green is slow enough to allow the use of this dye as the stationary phase counter-ion.

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DIBROMAMINE-B AS A NEW REDOX TITRANT IN NON-AQUEOUS OR PARTIALLY AQUEOUS MEDIA

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Summary—A new redox titrant, dibromamine-B (*N*,*N*′-dibromobenzene sulphonamide) is introduced for use in acetic acid medium. Direct potentiometric determinations of hydrazine, ascorbic acid, aniline, thiourea and its metal complexes and oxine and its metal complexes have been described.

The number of suitable oxidants available for non-aqueous redox titrimetry is limited. Recently, organic haloamines have received considerable attention as redox titrants. Although the well-known members of this class, namely, chloramine-T and chloramine-B are soluble in water, dichloramine-T (DCT)[1–5] and dibromamine-T (DBT)[6,7] are employed as redox titrants in non-aqueous or partially aqueous media. A recent addition to the group is dibromamine-B (*N*,*N*′-dibromobenzene sulphonamide, hereafter abbreviated to DBB) which can be used as an oxidimetric titrant in acetic acid medium. Potentiometric determinations of typical, yet diverse, reductants such as hydrazine, ascorbic acid, aniline, thiourea and its metal complexes and oxine and its metal complexes, have been carried out with this new redox titrant and these results are reported in the present communication.

EXPERIMENTAL

Apparatus

A Bajaj potentiometer with a platinum indicator electrode and a reference calomel electrode was used for potentiometric titrations. All titrations were done at room temperature (25 ± 2°). End-points were determined by drawing normal, first-derivative and second-derivative curves.

Reagents

Dibromamine-B. DBB was prepared by the bromination of chloramine-B (CAB). Pure chlorine gas was bubbled through a solution of benzene sulphonamide in 4*M* sodium hydroxide over a period of 1 hr at 70°. The chloramine-B obtained was filtered off, dried and recrystallized from water. CAB (30 g) was dissolved in water (560 ml) and liquid bromine (6 ml) was added dropwise from a burette with constant stirring. The yellow precipitate of DBB formed was thoroughly washed with water, filtered under suction and dried in a vacuum desiccator: yield about 35 g, indicating ~100% recovery. The sample was stored in brown bottles. The dry sample melts at 110–111° with decomposition. The available bromine was determined by iodometry (found, 51.0%; theory, 50.74%).

Spectral analyses

The infrared spectra of CAB and DBB (in KBr discs) are almost the same, but DBB was further characterized by Fourier transform NMR ^{13}C and ^{1}H spectra (obtained on a Bruker-WH 270 NMR spectrometer, Switzerland). The proton-noise-decoupled ^{13}C spectrum (measured in methanol-d) showed the following chemical shifts (δ in ppm from Me_4Si): C-1 atom attached to S atom (143.285); C-2,2′ atoms (129.491); C-3,3′ atoms (126.205); C-4 atom (132.901). The ^{1}H spectrum (measured in $CDCl_3$; Me_4Si internal standard) showed three distinct peaks centred around 8.15 (doublet), 7.81 (triplet) and 7.67 δ (triplet) due to the *o*-, *m*- and *p*-protons respectively. The PMR signals due to *m*- and *p*-protons appear as a multiplet for the parent compound CAB, but the peaks are well resolved for DBB. A downfield shift of 0.3 and 0.1 δ has been observed for the *o*- and *m*-protons in DBB, with $J_{o,m}$ = 8.0 Hz. Comparison of the CMR spectra of DBB and CAB indicates an upfield shift for C-1 (~0.8 ppm) and a downfield shift of ~2 ppm for the other carbon atoms. In DBB, the introduction of a halogen atom thus increases the electron density around C-1 (carbon attached to the hetero atom) and it is likely that DBB may function as a better oxidizing agent than CAB.

Preparation and standardization of stock solutions of DBB

DBB is very slightly soluble in water (0.339 g/kg), but is fairly soluble in glacial acetic acid (160.6 g/kg) and other common organic solvents. The solubilities given are for 30°. An approximately 0.025*M* (~0.1*N*) solution of DBB was prepared by dissolving 7.88 g in a litre of water-free acetic acid and preserved in amber-coloured bottles. The solution was found to be fairly stable. The normality of a typical stock solution over a period of 15 days is given in Table 1.

DBB solutions decompose slightly when stored in colourless bottles exposed to light. Hence they are preserved in brown bottles and for accurate work should be standardized daily (by addition of aqueous potassium iodide solution to aliquots of the oxidant and titration of the liberated iodine with thiosulphate).

Reductants

The compounds used were of analytical-reagent quality. Aqueous solutions of the following were prepared; hydrazine sulphate (~5 mg/ml); ascorbic acid (~2 mg/ml); aniline, redistilled (~5 mg/ml); thiourea (~2 mg/ml) and its complexes (~5 mg/ml). Thiourea complexes of zinc and

Table 1. Stability (normality) of dibromamine-B solutions in acetic acid

Number of days	0	1	2	3	4	5	6	7	15
Kept in amber bottle in dark	0.1023	0.1023	0.1023	0.1021	0.1021	0.1019	0.1019	0.1017	0.1009
Kept in amber bottle in daylight	0.1021	0.1021	0.1021	0.1017	0.1017	0.1014	0.1014	0.1009	0.09961
Kept in colourless bottle in dark	0.1023	0.1023	0.1021	0.1019	0.1019	0.1019	0.1017	0.1017	0.1005
Kept in colourless bottle in daylight	0.1023	0.0987	0.0967	0.0937	0.0915	0.0872	0.0847	0.0811	0.0616

cadmium were prepared by methods reported in the literature or by mixing the ligand and metal salt solutions in stoichiometric proportions, followed by evaporation and cooling. The purity of the complexes was checked by elemental analysis. A standard solution of oxine (~5 mg/ml) was prepared in 50% aqueous acetic acid. Anhydrous oxinates of Fe(III), Co(II), Zn(II), Cu(II), Ni(II) and Mg(II) were prepared by standard procedures. Solutions of the oxinates (~5 mg/ml) were prepared in 4*N* sulphuric acid (~2 mg/ml in the case of iron and nickel oxinates). The strengths of these solutions were checked by the bromate–bromide method.[8]

Procedure

Addition of potassium bromide was found essential in some cases although hydrazine and thiourea could be directly titrated with DBB. Ascorbic acid was titrated with DBB in presence of 0.5 ml of 10% potassium bromide solution and aniline, oxine and metal oxinates in presence of 10 ml of the bromide solution. About 1 g of potassium bromide had to be added during the titration of metal complexes of thiourea.

RESULTS AND DISCUSSION

A statistical evaluation of the results is given in Table 2.

In the vicinity of the end-point a steady potential was attained almost instantaneously in all cases. In this respect, DBB enjoys a clear advantage over DCT and DBT. The formal redox potential of the DBB–sulphonamide couple in acetic acid medium was determined by the extrapolation procedure and found to be +1.32 V at 25°.

In the case of ascorbic acid, aniline, thiourea complexes, oxine and oxinates, the actual oxidant seems to be bromine produced *in situ* by the reaction of the added potassium bromide with the oxidant. In these reactions, DBB is reduced to benzenesulphonamide.

$$RNBr_2 + 2H^+ + 4e \rightarrow RNH_2 + 2Br^-$$

(where R = $C_6H_5SO_2$).

Hydrazine and thiourea react directly with the oxidant as follows:

$$N_2H_4 + RNBr_2 \rightarrow N_2 + 2H^+ + 2Br^- + RNH_2$$

$$NH_2CSNH_2 + 2RNBr_2 + 5H_2O \rightarrow NH_2CONH_2 + 2RNH_2 + 6H^+ + SO_4^{2-} + 4Br^-.$$

Ascorbic acid is oxidized to dehydroascorbic acid with a two-electron change, while aniline is brominated to give tribromoaniline (m.p. 119°). Urea formed

Table 2. Potentiometric titrations of some reductants with dibromamine-B

Reductant*	Reductant taken, *mmole*	Coefficient of variation,† %	Range studied, *mg*	Error, %
Hydrazine sulphate	0.3845	0.4	100.0–5.0	0.2–0.8
Ascorbic acid	0.2839	0.3	100.0–5.0	0.2–0.9
Aniline	0.2938	0.2	54.7–10.9	0.6–1.0
Thiourea	0.2625	0.5	99.9–10.0	0.2–0.8
$Zntu_3SO_4$	0.0645	0.3	50.4–2.5	0.0–0.5
$Cdtu_2Cl_2$	0.0746	0.5	50.0–2.5	0.1–0.8
$Zntu_2(OAc)_2$	0.0745	0.4	25.0–2.5	0.1–0.7
$Cdtu_2(HCOO)_2$	0.0700	0.3	34.7–5.0	0.1–0.9
$Cdtu_2(OAc)_2$	0.0656	0.1	50.2–5.0	0.4–1.0
$Zntu_2Cl_2$	0.0869	0.2	50.1–2.5	0.0–0.7
Oxine	0.3447	0.5	100.0–15.0	0.2–0.9
$Fe(C_9H_6ON)_3$	0.1024	0.0	50.0–2.0	0.5–1.0
$Co(C_9H_6ON)_2$	0.1435	0.4	49.8–2.5	0.0–0.8
$Zn(C_9H_6ON)_2$	0.1422	0.4	50.3–2.5	0.0–0.8
$Cu(C_9H_6ON)_2$	0.1427	0.3	50.2–20.1	0.4–1.0
$Ni(C_9H_6ON)_2$	0.1443	0.3	50.1–20.0	0.2–0.8
$Mg(C_9H_6ON)_2$	0.1604	0.5	50.1–20.1	0.1–1.0

* tu = NH_2CSNH_2.
† Four replicates.

in the oxidation of thiourea was detected by the diphenylcarbohydrazide test.[9] Oxine undergoes a four-electron change and bromination to give dibromo-oxine. Benzenesulphonamide formed during these reductions was detected by TLC with a mixture of petroleum ether, chloroform and n-butanol (1:1:0.5 v/v) as the mobile phase and iodine as the detection agent ($R_F = 0.88$).

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QUINOLINE-2-ALDEHYDE THIOSEMICARBAZONE (QAT) AS SPECTROPHOTOMETRIC REAGENT FOR PALLADIUM AND NICKEL

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Summary—A procedure is described for the extractive spectrophotometric determination of nickel and palladium with quinoline-2-aldehyde thiosemicarbazone. At pH 7.5 nickel forms a 1:2 complex which is soluble in chloroform and has an absorption maximum at 460 nm. Palladium forms a 1:2 complex with maximum absorbance at 510 nm which can be extracted into MIBK from 1*M* HCl. Both complexes are stable and conform to Beer's law. The molar absorptivities for nickel and palladium are 1.58×10^4 and 2.6×10^3 $l.mole^{-1}.cm^{-1}$ respectively. The proposed method is suitable for detection and determination of nickel and palladium in the presence of associated metal ions. The results of the analysis of synthetic mixtures and standard samples are reported.

Quinoline-2-aldoxime has been used as spectrophotometric reagent for copper,[1] palladium[2] and rhenium.[3] Similarly, quinoline-2-aldehyde thiosemicarbazone (QAT)[4] forms coloured solutions with copper and nickel salts, but its utility as a spectrophotometric reagent for metal ions is still uninvestigated. This paper describes systematic studies on its use for solvent extraction and selective spectrophotometric determination of palladium and nickel.

EXPERIMENTAL

Reagents

Quinoline-2-aldehyde thiosemicarbazone (QAT). The reagent was synthesized by refluxing equimolar amounts of quinoline-2-aldehyde and thiosemicarbazide. A 0.1% solution of QAT (m.p. 234°) in 1:1 water–dimethylformamide mixture was used for nickel and a 0.01% solution in the same solvent was used for palladium determination.

Stock solution of nickel chloride $4.3 \times 10^{-2}M$.

Stock solution of palladium chloride $1.0 \times 10^{-2}M$. The stock solutions were standardized and solutions containing 5 ppm Ni and 50 ppm Pd were prepared by appropriate dilution.

All other chemicals used were of guaranteed grade.

Recommended extraction procedure

Take an aliquot of sample solution containing 5–25 μg of nickel, add 4 ml of 0.1% QAT solution and 2 ml of 1*M* aqueous pyridine solution and dilute to 20 ml with distilled water. Adjust the pH to 7.5 and make up to 25 ml. Transfer the solution to a separating funnel and after 10 min extract by shaking, for 15 sec each time, with two 5-ml portions of chloroform. Collect the lemon-yellow organic phase, dry it with anhydrous sodium sulphate and measure the absorbance at 460 nm against a reagent blank prepared in the same manner.

For the determination of palladium take an aliquot of solution containing 50–200 μg of palladium, add 4 ml of 0.01% QAT solution and enough hydrochloric acid to make its concentration 1*M* in a total volume of 10 ml. Transfer the solution into a 100-ml separating funnel and shake (for 1 min each time) with two 5-ml portions of MIBK. Collect the orange-red organic phase, dry it with anhydrous sodium sulphate and measure the absorbance of the complex at 510 nm against a reagent blank prepared in the same manner.

RESULTS AND DISCUSSION

Spectral characteristics and extraction conditions

The absorption spectrum of the Ni–QAT complex (10 μg of Ni) extracted into chloroform at pH 7.5 shows maximum absorbance at 460 nm. The reagent does not absorb at this wavelength. The system conforms to Beer's law over the nickel concentration range of 0.5–2.5 μg/ml in the organic phase, at 460 nm. The molar absorptivity of the complex is 1.58×10^4 $l.mole^{-1}.cm^{-1}$ at 460 nm. The colour is stable for 24 hr. The extraction is quantitative at pH 7.2–7.8 (Table 1). Variation in the concentration of QAT and pyridine showed that 4 ml of 0.1% QAT solution and 2 ml of 1*M* pyridine are adequate for complete complexation of 5–25 μg of Ni. Excess of reagent, however, has no adverse effect on the complexation and extraction. The extraction period for quantitative extraction is only 15 sec. The effect of

Table 1. Extraction of Ni–QAT complex (Ni 10 μg) as a function of pH

pH	4.5	5.0	5.5	6.0	6.5–7.0	7.2–7.8	8.0–8.5
Extraction, %	35.2	66.7	87.0	88.9	92.6	100.0	98.1

Table 2. Extraction of Ni–QAT and Pd–QAT complexes with various organic solvents

Solvent	Extraction %, Ni	Pd
Carbon tetrachloride	0.0	0.3
Benzene	0.0	8.3
Toluene	0.0	8.3
Xylene	0.0	4.2
Chloroform	100.0	38.7
Isoamyl alcohol	79.6	24.2
MIBK	38.9	100.0
Ethyl acetate	51.8	87.3

Ni = 10 μg; pH of aqueous solution = 7.5; Pd = 100 μg; acidity of aqueous solution = 1*M* HCl.

different organic solvents is shown in Table 2. The only effective solvent of the eight tested was chloroform.

The absorption spectrum of the Pd–QAT complex (100 μg of Pd) extracted into MIBK from 1*M* hydrochloric acid has an absorption maximum at 510 nm, the molar absorptivity being 2.6×10^3 $l.mole^{-1}.cm^{-1}$. Beer's law is obeyed over the palladium concentration range 2.5–20 μg/ml in the organic phase (at 510 nm) for the complex extracted from 1*M* hydrochloric or acetic acid. The complex is stable for 20 hr. The extraction is quantitative from 1–3*M* hydrochloric, acetic or sulphuric acid media (Table 3), but nitric acid is unsuitable. Four ml of 0.01% QAT solution and 15 sec shaking time is adequate for optimum colour development of the complex. Excess of reagent had no effect on the intensity of the colour. The results in Table 2 show that the only effective solvent for the quantitative extraction of the Pd–QAT complex is MIBK.

The precision of the method is fairly good (2.6–0.6% error for 20–5 μg of Ni; 1.2–0.7% for 150–50 μg of Pd).

Effect of foreign ions

A number of representative ions were examined for their interference in the determination of nickel and palladium by the recommended procedure. The tolerance limit (Table 4) was set at the amount required to cause 1% error. The study showed that of the ions tested the only serious effect is by Cd(II) and Pd(II) on the Ni determination and by Au(III), Pb(II), and SCN^- on that of Pd.

Table 3. Extraction of Pd–QAT complex (Pd 100 μg) as a function of acidity

Acid	Extraction, %
0.25*M* HCl	77.1
0.5*M* HCl	95.9
1–3*M* HCl	100.0
4*M* HCl	93.7
1–3*M* CH_3COOH	100.0
1–3*M* H_2SO_4	100.0
1–3*M* HNO_3	50.0

Table 4. Effect of foreign ions on extraction of Ni (10 μg) and Pd (100 μg)

Ions added	Tolerance limit, *mg* Ni	Pd
Ag(I)	0.1	2.0
Cu(II)	0.1	0.1
Co(II)	0.3	3.0
Zn(II)	0.1	2.0
Cd(II)	Nil	3.0
Mn(II)	0.5	4.0
Sn(II)	0.1	2.0
Ni(II)	—	0.5
Pd(II)	Nil	—
Al(III)	0.5	4.0
Bi(III)	2.5	—
Cr(III)	0.1	3.5
Au(III)	0.1	Nil
Sb(III)	0.1	0.1
Ru(III)	0.1	0.5
Rh(III)	0.1	2.0
Ir(III)	0.1	2.0
Fe(III)*	0.1	3.0
La(III)	—	5.0
Sn(IV)	1.5	0.1
Pt(IV)	0.1	0.5
Th(IV)	0.1	2.0
Se(IV)	—	2.5
Te(IV)	—	1.5
V(V)	0.5	3.0
U(VI)	—	5.0
Mo(VI)	2.5	4.0
W(VI)	1.5	0.5
Cr(VI)	0.5	0.5
Os(VIII)	—	3.0
Tartrate	5.0	5.0
Citrate	5.0	5.0
Ascorbate	5.0	5.0
EDTA	2.0	0.5
Phosphate	—	5.0
Fluoride	2.0	2.5

* Masked with EDTA.

Composition of extracted species

The composition of the Ni–QAT and Pd–QAT complexes were determined by Job's continuous[5] variation method and the mole-ratio method.[6] Both methods indicate the formation of a 1:2 complex.

Applications

Both nickel and palladium can be detected and determined in presence of associated metal ions. The results for various synthetic mixtures are reported in Table 5.

Determination of nickel in steel and nickel silver. Dissolve 500 mg of the steel sample (NBS) and 1 g of nickel silver as described elsewhere[7] and determine nickel by the proposed method in an aliquot of the solution. For the analysis of steel samples, iron is first selectively removed by extraction with mesityl oxide[8] or 4-methylpentan-2-ol[9] and nickel in the aqueous

Table 5. Analysis of synthetic mixtures (means of triplicate determinations)

Composition of mixture and amounts taken μg	Nickel recovered, %	Palladium recovered, %	Relative error, %
Ni, 10; Co, 100	99.4	—	0.6
Ni, 10; Cr, 100; Mn, 100; Mo, 100	98.3	—	1.7
Ni, 10; Cr, 100; Mn, 100; V, 100	99.0	—	1.0
Ni, 10; Cr, 100; Mn, 100; Mo, 100; Bi, 100	98.3	—	1.7
Ni, 10; Cu, 100; Mn, 100; Cr, 100; Mo, 100; Fe, 100 (masked with EDTA)	98.7	—	1.3
Ni, 10; Zn, 100; Bi, 100; Al, 100	99.0	—	1.0
Ni, 10; Mn, 100; Bi, 100; Zn, 100; Cu, 100	98.5	—	1.5
Pd, 100; Pt, 200	—	98.9	1.1
Pd, 100; Co, 100; Ni, 100	—	98.9	1.1
Pd, 100; Ir, 100; Rh, 100; Ru, 100; Os, 100	—	98.7	1.3

Table 6. Analysis of standard samples

Sample	Composition %	Nickel content, % Declared	Found	Relative error, %
Steel 33b (NBS)	C, 2.24; Si, 2.0, P, 0.11; S, 0.03; Mn, 0.64; Cr, 0.61; Mo, 0.40	2.24	2.20	1.8
Steel 33c (NBS)	C, 3.31; Si, 1.88; S, 0.06; P, 0.11; Mn, 0.86	1.98	1.96	1.0
Steel 33d (NBS)	C, 2.30; Si, 1.63; S, 0.02; P, 0.02; Mn, 0.63; Cr, 0.52; Cu, 1.54; Mo, 0.48;	2.38	2.34	1.7
Nickel silver	Mn, 0.27; Bi, 0.6; Cu, 55.1; Zn, 25.83	18.20	18.0	1.0

extract is determined by the proposed method. Results for the analysis of some standard samples are reported in Table 6.

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QUANTITATIVE PRECIPITATION OF LARGE AMOUNTS OF SODIUM AS SODIUM ZINC URANYL ACETATE AND ITS DETERMINATION BY AN INDIRECT COMPLEXOMETRIC METHOD

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Summary—Up to 40 mg of sodium can be quantitatively precipitated as sodium zinc uranyl acetate if enough reagent of appropriate composition is added to make the concentrations of zinc and uranium in the mother liquor at least 1.25 and 0.14*M* respectively. In practice, the reagent solution contains 100 g of uranyl acetate and 300 g of zinc acetate per litre and the volume added (ml) must be at least 15 times that of the solution to which it is added or 1.5 times the number of mg of sodium present, whichever is the greater. The triple salt can then be dissolved in water and the zinc selectively titrated with EDTA at pH 5.3, with Xylenol Orange as indicator. The uranium is masked with ammonium fluoride. Most constituents of ceramics and other silicates, including barium, strontium, magnesium, potassium, sulphate, phosphate and arsenate, do not interfere.

Sodium is present in most silicate materials, including glass and enamel. Sodium content less than 10% is usually determined by flame photometry.[1] When the sodium content is higher, the accuracy may be inadequate because of the dilution factor. Of the classical gravimetric methods, that using zinc uranyl acetate[2] is the most widely used, with minor modifications.[3–13] However, in most of these methods up to only 10.8 mg of sodium oxide is precipitated, from the test solution concentrated to 1 ml, with 3–10 ml of zinc uranyl acetate reagent. However, Koening[14] reported quantitative precipitation of up to 12.6 mg of sodium oxide from a solution concentrated to 5 ml, with 20 ml of the reagent solution. Thus the literature does not give a clear guidance on the conditions to be used.

The titrimetric methods reported in the literature are essentially based on separation by the zinc uranyl acetate method followed by a simple titrimetric finish such as (1) reduction of UO_2^{2+} to U^{4+} followed by an oxidimetric titration,[15,16] (2) alkalimetric titration,[17,18] (3) precipitation titration[19] and (4) titration of zinc with ferricyanide–iodide–thiosulphate[20] or EDTA.[21,22] The first three methods are adversely affected by co-precipitation of any uranyl compounds, in particular potassium uranyl acetate. The complexometric titration of zinc has been examined only for estimation of micro amounts of sodium up to 0.32 mg.

The present investigation was undertaken to find the conditions for quantitative precipitation of higher amounts of sodium as its triple salt and then to work out a simple indirect complexometric method for determination of sodium in glass and other silicate materials.

The study reveals that at room temperature (25 ± 5°) quantitative precipitation of up to 40 mg of sodium (54 mg of Na_2O) from 1–4 ml of test solution is possible when the concentrations of the excess of zinc and uranium in the mother liquor are 1.25*M* and 0.14*M* respectively. For practical purposes, the volume of reagent solution to be added must be at least 15 times the volume of the test solution or 1.5 times the number of milligrams of sodium present in the test solution, whichever is the greater.

EXPERIMENTAL

Reagents

Zinc uranyl acetate solution. Dissolve separately (by heating) 100 g of uranyl acetate in 300 ml of water containing 20 ml of glacial acetic acid, and 300 g of zinc acetate in 500 ml of water containing 15 ml of glacial acetic acid. Mix the hot solutions, keep them overnight, filter, dilute to 1 litre and store in a polythene bottle.

Standard zinc solution. Dissolve about 1.6 g of pure zinc metal (weighed accurately) in 6*M* hydrochloric acid and dilute to 1 litre. Calculate the molarity from the weight taken.

*EDTA solution, 0.025*M. Standardized against the standard zinc solution at pH 5.3, with Xylenol Orange as indicator.

Buffer solution (pH ~ 5.3). Dissolve 21.5 g of sodium acetate trihydrate in 500 ml of water containing 2 ml of glacial acetic acid and dilute to 1 litre.

Xylenol Orange. A 0.2% solution in water containing a drop of 6*M* hydrochloric acid.

Wash solution. Saturate 450 ml of absolute alcohol containing 4.5 ml of 30% acetic acid with sodium zinc uranyl acetate at room temperature (25 ± 5°).

Ammonium fluoride solution, 10%.

Procedure

Take up to 4 ml of test solution containing up to 40 mg of sodium in a 100-ml beaker. With stirring add zinc

uranyl acetate solution, using a volume (ml) at least 15 times the volume of the test solution or 1.5 times the number of mg of sodium, whichever is the greater, and continue stirring for a few minutes. Let the precipitate settle for 30–40 min. Filter off on a dry sintered-glass crucible (porosity 4) and wash the precipitate with two or three 5-ml portions of reagent solution, then 8–10 times with wash solution followed by acetone 2 or 3 times. Dissolve the precipitate in five 10 ml portions of water, collecting the solution quantitatively. Add 20 ml of buffer solution, 10 ml of ammonium fluoride solution and six drops of Xylenol Orange solution, then titrate the zinc with EDTA.

Sodium in glass and other silicate materials

Decompose 0.5 g of sample with 10 ml of hydrofluoric acid and 5 ml of perchloric acid in a platinum dish and heat to fuming. Add another 10 ml of hydrofluoric acid and heat to fuming again. Take up in water, transfer to a 100-ml standard flask and make up to volume. Take a fraction containing up to 40 mg of sodium, evaporate it to a syrupy consistency and then diluted to 2–4 ml with water. Determine the sodium as described above.

Calculation

Na = $A \times B \times 351.8$ mg where A = ml of EDTA consumed in the titration, B = g of zinc equivalent to 1 ml of EDTA.

RESULTS AND DISCUSSION

According to the law of mass action, the completeness of sodium precipitation as zinc uranyl acetate will depend on the concentrations of zinc and uranium ions in the mother liquor. The effect of the reagent solution on the precipitation of up to 40 mg of sodium was therefore critically studied. From the results in Table 1, it is clear that virtually quantitative precipitation was achieved in experiments 2–7 where the minimum concentrations of zinc and uranium ions in the mother liquor were 1.25 and 0.14*M* respectively. In all other cases negative errors, increasing with decrease in the zinc or uranyl ion concentration, were obtained because of incomplete precipitation of sodium. These observations suggest that the minimum concentrations of zinc and uranium in the mother liquor for quantitative precipitation of sodium are 1.25 and 0.14*M* respectively. The practical condition is that the necessary volume of reagent with uranyl acetate and zinc acetate concentrations of 100 and 300 g/l respectively is at least 15 times the volume of sample solution, or its volume in ml must be at least 1.5 times the number of mg of sodium present, whichever is the greater. It is not essential to concentrate the sample solution to 1 ml prior to the addition of reagent solution, as recommended by most of the earlier workers,[3–13] as this might cause undesired precipitation of certain salts. However, for practical reasons, and in very precise work, the volume of sample solution should be kept below 5 ml.

The procedure worked out is based on the observations above, and up to 40 mg of sodium can be precipitated quantitatively, and indirectly determined by dissolving it and titrating the zinc with EDTA at pH 5.3, Xylenol Orange being used as indicator and uranium(VI) masked with ammonium fluoride. Use of dithizone as indicator[21] was found to produce sometimes erratic results in presence of ethyl alcohol.

The method is practically free from interference. Calcium, barium, strontium and magnesium (up to 240 mg), which interfere with gravimetric methods[3–13] and complexometric titrations at pH 10,[20,21] do not have any adverse effect on the present method since they do not form stable complexes with EDTA at pH 5.3. Potassium, which yields positive errors in gravimetric[2–14] and oxidimetric methods[15,22] by precipitating as potassium uranyl acetate, does not interfere in the present method. The interference caused by hydrolysis of cations such as Ti(IV), Fe(III) and Al(III) during washing of the sodium precipitate is eliminated by first washing with acidic wash solution.

Table 1. Effect of reagent concentration on the determination of sodium

Expt.	Na solution taken, *ml*	Reagent: Na solution *v/v*	Weight of sodium, *mg*: Taken	Found*	Difference, %	Molarity in mother liquor, *M*: Uranium	Zinc
1	1	10	8.0	7.98	−0.3	0.12	1.21
2	5	15	10.0	10.04	+0.4	0.20	1.27
3	1	15	10.0	10.02	+0.2	0.14	1.25
4	1	20	15.0	15.06	+0.4	0.13	1.27
5	2	15	20.0	20.02	+0.1	0.14	1.26
6	3	15	24.0	24.04	+0.2	0.16	1.26
7	4	15	40.0	40.03	+0.1	0.14	1.25
8	5	4	8.0	7.93	−0.9	0.14	1.08
9	5	4	10.0	9.90	−1.0	0.14	1.076
10	1	10	10.0	9.75	−2.5	0.10	1.20
11	1	10	15.0	14.03	−6.6	0.04	1.18
12	1	15	15.0	14.86	−0.9	0.098	1.24
13	2	10	20.0	19.80	−1.0	0.095	1.20
14	3	10	24.0	23.90	−0.4	0.12	1.21
15	4	10	40.0	39.76	−0.6	0.10	1.20
16	4	12	40.0	39.86	−0.4	0.12	1.23

* Mean values of three determinations are presented.

Table 2. Determination of Na_2O in glass and related materials

Sample	Na_2O, %	Mean, %	Certified value, %
Sodium aluminate (SiO_2 4.69, Al_2O_3 60.0, Fe_2O_3 0.20, K_2O 1.02.)	32.97 32.91 32.83	32.90	32.95
Felspar (NBS) 99a* (SiO_2 65.20, Al_2O_3 20.50, TiO_2 0.007, Fe_2O_3 0.06, CaO 2.14, MgO 0.02, BaO 0.26, K_2O 5.2, P_2O_5 0.02.)	6.20 6.28 6.30	6.26	6.30
Enamel I (SiO_2 53.55, Al_2O_3 8.37, TiO_2 trace, Fe_2O_3 0.06, CaO 4.12, MgO 1.0, B_2O_3 14.25, K_2O 4.04)	14.75 14.60 14.75	14.70	14.65
Enamel II (SiO_2 55.48, Al_2O_3 6.36, TiO_2 trace, Fe_2O_3 0.50, CaO 3.20, MgO 0.40, BaO 0.36, B_2O_3 14.54, K_2O 4.30)	14.72 14.80 14.76	14.76	14.80
Frit (SiO_2 47.33, Al_2O_3 1.06, TiO_2 1.02, Fe_2O_3 0.02, CaO 7.30, MgO 0.38, BaO 15.60, B_2O_3 1.41, K_2O 4.30)	21.21 21.23 21.30	21.24	21.30
Coloured glass tiles (SiO_2 65.19, Al_2O_3 2.1, TiO_2 trace, Fe_2O_3 0.13, CaO 2.41, ZnO 6.60 CdO 0.44, K_2O 4.95, S 0.81)	17.70 17.63 17.70	17.67	17.70

* Values from N.B.S. provisional certificate.

The method has been applied for accurate determination of sodium in commercial sodium aluminate, glass and other silicate materials after decomposition of the sample with hydrofluoric and perchloric acids as described in the procedure. The results compare favourably with certified values (Table 2).

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ANALYTICAL DATA

CORRECTION FACTORS FOR THE GLASS ELECTRODE IN AQUEOUS METHANOL

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In a previous communication we gave the data for conversion of pH measurements in aqueous dioxan media into hydrogen ion concentration.[1] So far there are no corresponding data available in the literature for aqueous methanol. In view of this in the present paper the values of log U_H and log U_H^0 at 25° (Table 1) for aqueous methanol are reported.

Table 1. Determination of log U_H and log U_H^0*, at 25°
$[HClO_4] = 0.0088M$
$[NaClO_4] = 0.0103M$

MeOH, %	Mole fraction of MeOH	log U_H	log $1/\gamma_\pm$	log U_H^0
0	0	−0.060	0.060	0
10	0.047	−0.015	0.063	0.05
20	0.100	+0.005	0.066	0.07
30	0.160	+0.060	0.070	0.13
40	0.228	+0.060	0.079	0.14
50	0.307	+0.135	0.090	0.23
60	0.400	+0.185	0.105	0.29
70	0.508	+0.195	0.122	0.32

* $-\log [H^+] = B + \log U_H$ where B is the pH, and $\log U_H = \log U_H^0 - \log 1/\gamma_\pm$ ($\gamma_\pm$ is the mean activity coefficient of hydrochloric acid under the conditions in which U_H determined). The values of B were the average of five independent measurements on solutions of the same nominal composition; log $1/\gamma_\pm$ values were calculated by interpolation from data given by Harned and Thomas[5] and by Nonhebel and Hartley.[6] The value $-\log [H^+] = 2.115$ was taken as pH $-\log 1/\gamma_\pm$ for aqueous solution.

The methanol was purified[2] and the procedure for the determination of log U_H and log U_H^0 was essentially that of Van Uitert,[3,4] used earlier.[1]

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ANNOTATIONS

SYNTHESIS OF THE ANALYTICAL LIGAND 2-tert.-BUTYL-8-HYDROXYQUINOLINE

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Summary—Two methods for the synthesis of 2-tert.-butyl-8-hydroxyquinoline are described. One involves a direct reaction of the parent compound with tert.-butyl-lithium, and the other is based on a cyclization reaction of *o*-aminophenol with 3-chloro-4,4-dimethylpent-2-enal. Physical data confirming the structure of the compound are presented.

The derivatives of the chelating ligand 8-hydroxyquinoline have been used extensively in many aspects of analytical chemistry. For example, of the 2-substituted compounds the methyl derivative has for some time been considered a possible reagent for the separation of Al(III) from other metal cations in aqueous solution. Recent work has shown that Al(III) in fact does form 1:3 chelates with this reagent in such media.[1,2] As a result, there has also been interest in the preparation and potential analytical significance of other 2-alkylated 8-hydroxyquinolines, particularly the 2-tert.-butyl derivative (2TBH). An attempt at the synthesis of 2TBH by Kaneko and Ueno[3] was based on a route involving reaction of the parent compound with tert.-butyl-lithium but was not successful. This result contrasts greatly with the observation that relatively high yields of the compound, a white crystalline material, could be obtained by a similar procedure.[4] In the present note, we wish to provide the details of a preparation of this potentially valuable reagent that is based on a β-chlorovinylaldehyde–amine reaction,[5] and of our findings concerning the nucleophilic substitution method.

EXPERIMENTAL

2TBH from tert.-butyl-lithium

8-Hydroxyquinoline (1 g) dissolved in 30 ml of diethyl ether was added slowly to 0.6 g of tert.-butyl-lithium in 100 ml of diethyl ether at −30°. After the mixture had been stirred at room temperature overnight, the product was extracted with warm dilute hydrochloric acid. The extract was neutralized and re-extracted with several small amounts of diethyl ether. Evaporation of the solvent yielded a dark red oil which was purified by preparative TLC. The resulting pale yellow oil (yield 3.4%) was confirmed as 2TBH by PMR, elemental analysis, mass spectrometry and UPS (see below).

A similar synthesis using 8-methoxyquinoline as a starting compound followed by appropriate demethylation resulted in a significantly greater yield of 2TBH (15%).

2TBH from 3-chloro-4,4-dimethylpent-2-enal

The precursor for the synthesis, 3-chloro-4,4-dimethylpent-2-enal, was prepared by a Vilsmeier reaction as follows.[6] Dimethylformamide (110 ml) was added slowly to 100 ml of phosphorus oxytrichloride at 0°. After stirring of the mixture for 1 hr, 40 ml of tert.-butyl methyl ketone were added dropwise and the mixture was stirred overnight at room temperature. The orange mixture was poured slowly onto crushed ice and then neutralized by additions of sodium bicarbonate. The oily product was extracted with diethyl ether, worked-up and then purified by vacuum distillation (65–68°/15 mmHg). The structure of the β-chlorovinylaldehyde was confirmed by PMR and mass spectrometry.

An excess of 3-chloro-4,4-dimethylpent-2-enal in 50 ml of n-butanol was added to *o*-aminophenol in the same solvent at room temperature. After refluxing at 140° for several hours, solvent removal, treatment with concentrated sodium hydroxide solution and neutralization with acetic acid, the mixture was subjected to work-up and partial purification by vacuum distillation. The two major fractions, boiling at 60–80° and 100–120° (1.5 mmHg), were further purified by column chromatography and vacuum distillation. The lower boiling fraction (a yellow oil) of 28% yield (based on the phenol taken) was identified as 2-tert.-butyl benzoxazole. The other fraction was a pale yellow oil and confirmed as 2TBH (9% yield).

RESULTS AND DISCUSSION

The products derived from the two routes to 2TBH described above gave identical analytical data. The mass spectrum contained the expected peaks at 201, M (55%); 186, M − CH_3 (base peak); 159, M − $C(CH_3)_2$ (17%); 145, M − $C(CH_3)_3$ (11%); and 117, M − CO − $C(CH_3)_3$ (8%). The PMR spectrum exhibited the typical AX spectrum for the H_3 and H_4 protons of the pyridine-ring at chemical shifts of 7.57 and 8.10 ppm, respectively. These values are within the ranges for the corresponding protons of other derivatives, *viz.* H_3 7.3–7.89 ppm and H_4 7.94–8.90 ppm; also, the $J_{3,4}$ coupling constant of 8.5 Hz is in agreement with the published value.[7] In the low ionization potential range of 8–11 eV the photoelectron spec-

trum exhibits the expected bands as follows; the values in brackets refer to the parent compound: Π_1, 8.05 eV (8.14); n, 9.16 eV (9.25); Π_2, 9.95 eV (9.96); and Π_3, 10.78 eV (10.50). Finally, the analytical data were as follows (expected values in brackets): C, 78.1% (77.58); N, 7.1% (6.96); H, 7.9% (7.51).

The production of the benzoxazole derivative from cyclization of the imino–enamine product derived from the β-chlorovinylaldehyde–amine condensation is particularly interesting in the light of the published mechanism for this reaction.[5] Clearly, cyclization involving the phenolic oxygen appears to be a preferred reaction to that producing the quinoline system.

Finally, the results of this work are essentially in agreement with the findings of Kaneko and Ueno concerning the very low yields of product obtained by nucleophilic substitution. Undoubtedly, this is related to the instability of the tert.-butyl carbanion. In the light of this work the high yields achieved by Kazi are puzzling.[4] Also, we are not able to corroborate the physical data given by this worker for 2TBH.

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* We wish to correct reference 9 in this paper—the page number should be 1487.

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RECOVERY OF SILVER FROM SILVER CHLORIDE RESIDUES

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Summary—A new chemical process for recovering silver metal from waste silver chloride residues is described. The silver chloride is digested in an oxidizing mixture before complexation with ammonia. High-purity free silver metal is precipitated from solution by the addition of ascorbic acid as the reducing agent.

Many analytical laboratories routinely discard considerable quantities of silver chloride, a practice that is wasteful and possibly environmentally hazardous. Numerous methods have been reported for the recovery of silver metal from waste,[1–6] but most suffer from a number of disadvantages. The primary variation in this process is in the type of reductant used. This note reports the use of ascorbic acid as the reducing agent.

EXPERIMENTAL

Silver chloride waste (from Mohr titrations and contaminated with meat by-products) was obtained from a local meat-processing plant.

The silver chloride suspension (0.5 litre) was acidified with 1–2 ml of concentrated hydrochloric acid and 50 ml of concentrated nitric acid, and digested at 100° with gentle stirring until the residue appeared white and the supernatant liquid was light green. Saturated potassium permanganate solution was added to the boiling mixture until a brown colour persisted for about one minute. Heating was continued until the brown colour dissipated. After cooling, the supernatant liquid was decanted and the silver chloride was filtered off on Whatman No. 541 paper on a Büchner funnel.

The silver chloride was transferred to a beaker and stirred while 28–30% ammonia solution was added until dissolution was complete. Then 0.94*M* ascorbic acid was added until no more silver was formed.

The silver was allowed to settle and the ammoniacal solution was decanted and saved for reuse. The silver was filtered off on Whatman No. 41 paper in a 30-cm Büchner funnel and washed with three 0.5-litre portions of demineralized water.

The silver was allowed to dry in air for 48 hr on the filter paper before being transferred to an alundum crucible coated with a borax flux. The crucible was placed in a muffle at 1200°. When melting was complete (within 30 min), the metal was poured into a 2-litre beaker of ice-water. The yield was 50.5 g of silver metal in the form of small beads.

The efficiency of this method was determined by processing a known quantity of silver chloride: 18.39 g required 190 ml of 28–30% ammonia solution for dissolution, and 54 ml of 0.94*M* ascorbic acid for complete precipitation. The amount of silver recovered after refining was 13.7 g (99.3%).

DISCUSSION

The redox potential of ascorbic acid is pH-dependent and ranges from +0.127 V at pH 4 to +0.34 V at a pH of 7, and may be greater at higher pH. Ascorbic acid is capable of reducing silver ions at any pH from 4 to 7 or higher since the standard reduction potential for the silver ion is +0.8 V. The reaction is found to be fast and quantitative.

Other chemicals often used[1,3,7] in the recovery of silver were found to have numerous disadvantages. Sodium sulphide, used for the initial separation of silver, forms insoluble silver sulphide. This process can be dangerous in acidic medium and additional steps in the recovery procedure are required.

Reduction with zinc, steel wool, or sodium borohydride is found difficult to control, and the silver produced is often contaminated. Hydroquinone produces silver particles less than about 8 μm in size, which causes problems in filtration because of clogging. Hydrolyzed sugar solutions[8] do not seem very effective.

With pure silver solutions, ascorbic acid gives silver particles larger than 8 μm, but typical silver chloride wastes are frequently contaminated with chromate indicator, fats, proteins, or other organic materials. These impurities lead to the formation of a much smaller particle size and must be removed. The silver chromate can be converted into the chloride by the addition of hydrochloric acid and the organic materials wet-oxidized with nitric acid and potassium permanganate.

CONCLUSION

The advantages offered by this method are simplicity and its use of inexpensive reagents and equipment. The product is pure and recovery is quantitative with all effluents being biodegradable. The process is applicable to any system yielding silver chloride or bromide, or to silver cyanide electroplating

solutions. The usual procedure for plating solutions involves the precipitation of silver chloride by the addition of sodium hypochlorite[5] followed by as many as six additional steps. With the ascorbic acid procedure, only three steps may be needed.

Silver may also be reclaimed from out-of-date films and photographic papers after complexing with ammonia, thereby avoiding a pyrolysis step. Silver can also be recovered from photographic bleaches and fixers, but the amount of ammonia required makes this uneconomical since the silver concentration in these solutions is very low.

The process, which has been granted a United States Patent,[9] can also be used for gold, palladium and mercury. Platinum should also be recoverable, but a successful procedure has yet to be worked out.

Care must be exercised when working with solutions of silver and ammonia because of potential formation of the highly explosive "fulminating silver", (Ag_3N or AgH_2N)[10] if they are allowed to dry out or remain standing for long periods of time. However, with reasonable care and immediate precipitation with ascorbic acid, no hazard should exist.

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THE USE OF APPROXIMATION FORMULAE IN CALCULATIONS OF ACID–BASE EQUILIBRIA—I

MONO- AND DIPROTIC ACIDS AND BASES

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Summary—The pH of mono- and diprotic acids is calculated by use of approximation formulae and the theoretically exact equations. The regions for useful application of the approximation formulae (error <0.02 pH) have been identified.

Several approximation formulae have been presented for calculation of pH in acid–base equilibria.[1,2] The papers in this series compare the solutions of the theoretically exact equations and the approximation formulae over a wide range of concentrations and dissociation constants, and identify the regions in which the approximation formulae give the pH correctly within ±0.02 pH unit, corresponding to ±5% error in hydrogen-ion concentration.[3] This paper deals only with pure solutions of single acids.

THEORY

Monoprotic acids

For a monoprotic acid with dissociation constant K_A, and analytical concentration C_A, material balance gives

$$C_A = [HA] + [A^-] \quad (1)$$

and charge balance gives

$$[H^+] = [OH^-] + [A^-]. \quad (2)$$

These equations give

$$K_A = \frac{[H^+]([H^+] - [OH^-])}{C_A - ([H^+] - [OH^-])}. \quad (3)$$

In the case of a strong acid, the term [HA] in equation (1) is ignored. Substituting C_A for $[A^-]$ in equation (2) gives

$$[H^+]^2 - C_A[H^+] - K_w = 0 \quad (4)$$

which leads to

$$[H^+] = \frac{C_A + \sqrt{C_A^2 + 4K_w}}{2}. \quad (5)$$

In the case of weak acids, the term $[OH^-]$ in equation (3) is neglected. This provides the approximate equation

$$[H^+]^2 + K_A[H^+] - K_AC_A = 0 \quad (6)$$

and the solution

$$[H^+] = \frac{-K_A + \sqrt{K_A^2 + 4K_AC_A}}{2}. \quad (7)$$

Ignoring the second term in equation (6) provides the simplest approximation formula:

$$[H^+] = \sqrt{K_AC_A}. \quad (8)$$

For very weak acids both $[H^+]$ and $[OH^-]$ are neglected in the denominator of equation (3). This provides the approximate solution

$$[H^+] = \sqrt{K_AC_A + K_w}. \quad (9)$$

Equation (3) yields the exact equation

$$[H^+]^3 + K_A[H^+]^2 - (K_AC_A + K_w)[H^+] - K_AK_w = 0. \quad (10)$$

Diprotic acids

For diprotic acids with successive dissociation constants K_1 and K_2, material balance gives

$$C_A = [H_2A] + [HA^-] + [A^{2-}] \quad (11)$$

and charge balance

$$[H^+] = [OH^-] + [HA^-] + 2[A^{2-}]. \quad (12)$$

These equations give the following approximation formulae. If K_A in equation (8) for monoprotic acids is replaced by K_1,

$$[H^+] = \sqrt{K_1C_A} \quad (13)$$

$$[H^+] = \frac{-K_1 + \sqrt{K_1^2 + 4K_1C_A}}{2}. \quad (14)$$

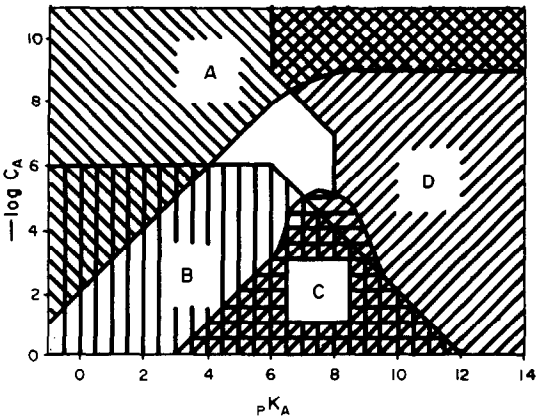

Fig. 1. Conditions for which the approximate formulae for monoprotic acids give the pH with error ≤0.02. (A) equation (5); (B) equation (7); (C) equation (8); (D) equation (9). In the unshaded island none of the formulae is applicable. The figure applies to monoprotic bases if K_A is replaced by K_B and C_A by C_B.

Addition of the hydrogen-ion contribution from the second dissociation step modifies equations (13) and (14) to

$$[H^+] = \sqrt{K_1 C_A} + K_2 \qquad (15)$$

$$[H^+] = \frac{-K_1 + \sqrt{K_1^2 + 4K_1 C_A}}{2} + K_2. \qquad (16)$$

Omission of the term $[OH^-]$ in equation (12) yields

$$[H^+]^3 + K_1[H^+]^2 + (K_1K_2 - K_1C_A)[H^+] - 2K_1K_2C_A = 0. \qquad (17)$$

The exact equation is

$$[H^+]^4 + K_1[H^+]^3 + (K_1K_2 - K_1C_A - K_w)[H^+]^2 - (K_1K_w + 2K_1K_2C_A)[H^+] - K_1K_2K_w = 0. \qquad (18)$$

Calculations

Calculation was done with a Casio fx-201P programmable electronic calculator. The value 1×10^{-14} was used for the ionic product of water. When the cubic or quartic equations were to be solved, values obtained from the approximate formulae were used as the initial estimates for successive refinement until the absolute least values were obtained. The results are shown in Table 1.

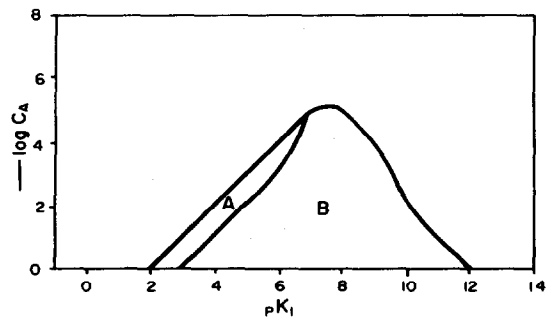

Fig. 2. Range of application of equation (13), (A) and (B) for $K_2/K_1 = 0.1$; (B) for $K_2/K_1 \leqslant 10^{-2}$.

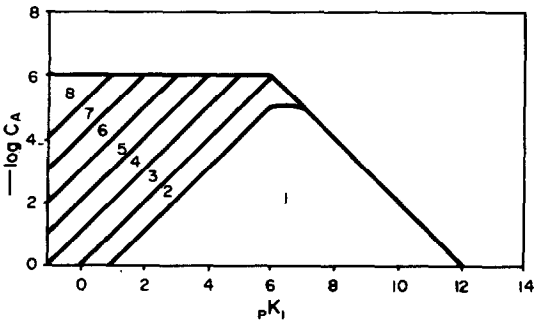

Fig. 3. Range of applicability of equation (14); (1) for $K_2/K_1 = 0.1$; (1) and (2) for $K_2/K_1 = 10^{-2}$; (1)–(3) for $K_2/K_1 = 10^{-3}$ *etc.*

Table 1. The pH values of a monoprotic acid having $pK_A = 0$ [the figures enclosed are within ±0.02 of the pH given by equation (10)].

$-\log C_A$	Eq. (8)	Eq. (5)	Eq. (7)	Eq. (9)	Eq. (10)
0	0.000	0.000	0.209	0.000	0.209
1	0.500	1.000	1.038	0.500	1.038
2	1.000	2.000	2.004	1.000	2.004
3	1.500	3.000	3.000	1.500	3.000
4	2.000	4.000	4.000	2.000	4.000
5	2.500	5.000	5.000	2.500	5.000
6	3.000	5.996	6.000	3.000	5.996
7	3.500	6.791	7.002	3.500	6.791
8	4.000	6.978	8.022	4.000	6.978
9	4.500	6.998	9.301	4.500	6.998
10	5.000	6.998		5.000	7.000

RESULTS AND DISCUSSION

Monoprotic acids

Figure 1 shows the conditions for which equations (5)–(9) give results differing by ≤0.02 pH unit from those obtained from equation (10).

Clearly most cases can be dealt with by using equation (7) for $C_A > 10^{-6}M$ and $pK_A < 6$, equation (5) for $C_A < 10^{-6}M$ and $pK_A < 4$ or for $C_A < 10^{-9}M$ and $pK_A > 4$, equation (9) for $pK_A > 8$ and any value of C_A. There is a small range of combinations of C_A and pK_A for which none of the approximations is useful. Equation (8) is of very limited value.

These considerations apply equally to monoprotic bases if K_A is replaced by K_B, C_A by C_B and $[H^+]$ by $[OH^-]$.

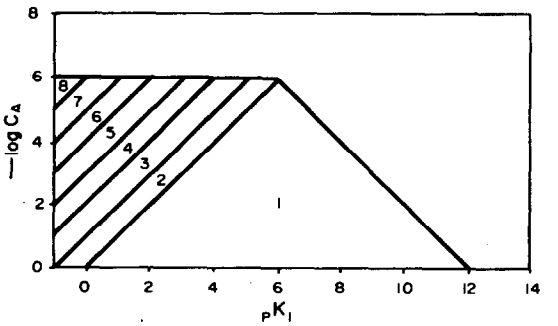

Fig. 4. Range of applicability of equation (16); (1) for $K_2/K_1 = 0.1$; (1) and (2) for $K_2/K_1 = 10^{-2}$; (1)–(3) for $K_2/K_1 = 10^{-3}$ *etc.*

Diprotic acids

Figure 2 shows the range of applicability of equation (13) [to give results within 0.02 pH unit of the value given by equation (18)]. The range depends on K_2/K_1. When this ratio is 0.1, the range covers both areas (A) and (B), but if this ratio is less than 0.01 only area (B) applies and is the same as area (C) in Fig. 1, derived from equation (8). As shown in Fig. 3, the range of application of equation (14) spreads out as K_2/K_1 decreases, becoming the same as area (B) in Fig. 1 when K_2/K_1 becomes 10^{-8}. This indicates that diprotic acids effectively behave as monoprotic acids if $K_2/K_1 \leqslant 10^{-8}$. Equation (15) gives the same result as equation (13), the borderline not being affected by the term K_2 in equation (15). Figure 4 shows that equation (16) gives the same result as equation (14) except for the shift of one unit in both pK_1 and log C_A for a given ratio of K_2/K_1. When this ratio reaches 10^{-8}, the range is described by area (B) in Fig. 1.

The range for use of equation (17) is not affected by the ratio K_2/K_1 and is the same as the total area delineated in Fig. 4.

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CARL FRIEDRICH MOHR AND ANALYTICAL CHEMISTRY IN GERMANY

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Summary—A brief account is given of the work of Mohr, which is set against the framework of the development of analytical chemistry in Germany from early times up to the present.

Carl Friedrich Mohr was born on 4 November 1806 in Koblenz, and died on 28 September 1879. Several biographical sketches have appeared,[1–5] and his long correspondence with Liebig has been collected and published with a biographical note.[6] The author of some 250 papers and numerous books, he has been called[1] the "Father of Volumetric Analysis", but his work extended far beyond this field, though it is for his contributions to analysis that he is usually remembered.

Mohr was a brilliant student, graduating *summa cum laude* in pharmacy, which was then rather a severe discipline, but instead of a university career chose to continue in pharmacy and run his father's business in Koblenz. At that time scientific research in Germany was regarded as the prerogative of the universities and professors, so Mohr would have been working outside official scientific circles. To some extent this disadvantage must have been offset by Mohr's long friendship with Liebig, and it was at Liebig's suggestion that Mohr asked about a professorship at Bonn, but failed to follow it up in time. When the failure of his business eventually forced him into teaching, it was Bonn that finally gave him his chair.

Mohr undoubtedly had great inventiveness, and Mohr's salt (ferrous ammonium sulphate), the Mohr method of argentometric chloride titration, the pinch-clamp, the Mohr burette (with a small bead inside a rubber tubing connection for improved control of outflow) have enshrined his name in the form of "household" words in analytical chemistry. Besides his own original researches, his great contribution to analysis was the publication of his famous textbook "Lehrbuch der chemisch-analytischen Titrirmethode", which appeared in two parts in 1855 and 1856, and reached its eighth edition in 1913. He made a critical examination of many titrimetric methods, introducing improvements of his own, before incorporating them into this outstanding manual of practical instruction. Because of the few references given in the book, the text frequently gives the impression that Mohr is describing his own discoveries, whereas the credit really belongs to others. Back-titration is an example. It is difficult, of course, to decide how far such instances are genuine rediscoveries made in ignorance of earlier work, and how far they are due to failure to acknowledge sources (a problem that exists even today[7]). Black, for example, had described back-titration[8] before Mohr was born, and though Mohr might well have been ignorant of this paper (though it had been mentioned by Klaproth[9]), it is less likely that he was unaware of Péligot's paper.[10] It is interesting to note that this paper was presented at a meeting of the French Academy of Sciences on 29 March 1847, and a translation[11] appeared in the issue of the *Chemical Gazette* for 1 May 1847—a feat that appears to be beyond the resources of modern abstracting services! Similarly Mohr appears to claim invention of normal solutions, though this is usually attributed to Ure,[12] or Griffin,[13] and Szabadváry[14] quotes Duflos as using in 1845 a normal solution[15] (though he may not have realized it himself). However, in the 7th edition of the Lehrbuch, edited by Classen, it is firmly stated on p. 56 that the idea originated with Griffin, and use of normality certainly became more common after the appearance of Mohr's book. It has recently been discovered that in fact Griffin had known Mohr for many years,[16] and presumably they discussed the idea.

Whatever the truth of the matter, Mohr himself has suffered from misattribution or rediscovery of his ideas. For example, it was Mohr who invented the Liebig condenser,[17] and Liebig only publicised it. Again, Mohr originated the idea of amplification reactions, oxidizing iodine to iodate with chlorine, the excess of which was boiled off before the addition of iodide and titration of the iodine liberated.[18] Curiously, Mohr was rather critical[19] of Schwarz's use of thiosulphate[20] as a titrant for iodine; time has proved him wrong.

Most of Mohr's ideas have amply stood the test of time, however, and some have a very modern ring to them. His method for folding filter papers[21] is the one still used, his invention of the cork-borer[23] and discovery of the efficacy of a mixture of turpentine and camphor as a lubricant for boring holes in glass[23] have been an everlasting boon to experimental chemistry, his method of sampling brown stone[24] is essentially the one still used, and his sale of standard solutions (at 10 groschen for a litre of 1 *N* nitric acid, the same as the price of a 10-ml burette or a 100-ml standard flask)[25] anticipated modern trends by about a century (Griffin also sold standard solutions and this is perhaps another aspect of his friendship with Mohr). Mohr's comments on over-elaborate methods being developed when simpler ones were obvious[26] will wake an echo in the minds of most referees and editors of present day papers.

Besides analytical chemistry, meteorology, mechanics, geology, bee-keeping and wine-growing all received contributions from Mohr, in the form of books and papers. Two of his less well known contributions are on the mechanical theory of heat.[27,28] One of these papers[27] appears with no author's name in the Jahresbericht written by Mohr for Liebig's *Annalen*, and is attributed to Mohr by Kahlbaum.[29] The other paper[28] was refused by both Liebig and Poggendorf but was accepted by Baumgartner in Vienna. Mohr himself did not know it had been published until 30 years later.[29,30] These two papers appeared five years before Mayer's paper which is often regarded as the first in the field. The record was finally set straight by Planck.[31]

Mohr was a sharp-tongued and argumentative character, severely critical of others, and it is possible that personal animosities may have led to some of his work being ignored; they certainly caused him difficulty, and there is a sad tale concerning Mohr's death.[32]

Mohr was undoubtedly endowed with a great gift for invention and innovation, and was perhaps the greatest individual worker in titrimetry. In many ways he was ahead of his time, and so failed to gain full recognition of his genius.

ANALYTICAL CHEMISTRY IN GERMANY

The history of analytical chemistry in Germany is in many ways a microcosm of the development of chemistry in general, and well illustrates the close ties between analysis and industry. It also raises speculation about the interaction of philosophy and analytical chemistry. The initial stages in the development of chemistry were necessarily occupied with gathering of facts and classification, and analysis was an essential part of the process. By its very nature, however, analysis is closely associated with numbers and quantification, and though Kelvin had a clear grasp of the prime importance of quantitative measurement, Kant had earlier announced that a true science was one that could be expressed mathematically, in the sense of abstract generalization.

Now it is well known to most practising scientists today that there is a difference between numeracy (the ability to perform arithmetic calculations correctly *and* to understand the significance of the numbers obtained) and mathematical ability (in the sense of understanding the logical relationships between numbers), and that there is a certain amount of class-distinction between the two. It is fashionable since the advent of the computer and the cheap pocket calculator to despise the ability to do arithmetical calculations and to venerate abstract mathematics as the "queen of the sciences" (a title that is also claimed by theology). It is plausible to suggest that it was the desire to make chemistry "respectable" by development of mathematical theory that led to the decline in status of analytical chemistry, as analysis was regarded as a mere number-gathering pursuit, and was regulated to a subordinate position, with little or no attempt to relate its practice to theory and vice versa. Even Ostwald, who was the first to attempt to put analysis on a sound theoretical basis, presumably thought in this way, since he said in the preface to his book "Die wissenschaftlichen Grundlagen der analytischen Chemie" that analytical chemistry is the servant of the other sciences, at the same time subordinate but also indispensable.[33]

Even today, when it is clear to those who can see (but not to those who will not) that correct analyses can only be consistently obtained if the underlying theory is thoroughly understood and properly applied, this attitude towards analysis persists in many academic circles, and it is perhaps not surprising that analysis is the Cinderella of chemistry (with no fairy godmother in sight). However, with the ever increasing demands made by modern technology and public opinion, there are signs of a resurgence of interest in analysis and Cinderella may yet come into her kingdom.

THE EARLY YEARS

As we have just said, analysis was the basis of early chemistry, and Germany was the scene of many important developments. Thus we may mention Georg Agricola (1494–1555) as one of the earliest workers in the field of mining and metallurgical analysis—a theme that recurs throughout the history of the subject and reflects the economic importance of analysis.

Water analysis was another topic extensively investigated, and the names of Leonhard Thurneysser (1530–1596, a student of Paracelsus), Andreas Libevius (1514–1616) and Friedrich Hoffman (1660–1743) span over a century of effort in this area. Johann Rudolf Glauber (1604–1670) made many observations in the course of production of chemicals on a commercial scale, including the solubility of silver chloride in ammonia. Around the same period Otto Tachenius was developing tests for metals, and

appears to have been a pioneer in biochemistry and toxicology.[34] He also observed that strong acids displace weak.

Most of the early work was necessarily qualitative, but an early piece of quantitative analysis was based on precipitation of silver chloride, by Johann Kunckel (1630–1703), who was also one of the pioneers of the blowpipe. This tool rapidly became indispensable in analytical work, and its use was extensively developed by Georg Ernst Stahl (1659–1734), Johann Cramer (1710–1777) and Sigismund Andreas Marggraf (1709–1782), who was one of the early workers at the celebrated Mining Academy at Freiberg. Some day we may be fortunate enough to have a history of this academy and its contributions to analysis. The sugar beet industry might well consider paying tribute to Marggraf for his discovery of the process for extracting the sugar. Another exponent of the blowpipe was Johann Heinrich Pott (1692–1777), who was engaged in an early example of industrial espionage in his attempts to find the composition of Meissen procelain.[35] Another name associated with the use of the blowpipe is Karl Friedrich Plattner (1800–1858), who was also at the Mining Academy. Goethe was taught to use the blowpipe by Berzelius.

Carl Freidrich Wenzel (1740–1793) worked at the mines in Freiberg, and was noted for the acccuracy of his experimental work. Wenzel is often given more credit for discovery than he is entitled to,[36] because later commentators have read into his work more than Wenzel had himself seen, and some of the credit must be shifted to Jeremias Benjamin Richter (1762–1831), who recognized the law of neutrality and established the principles of stoichiometry. However, Richter was unfortunately not an especially competent analyst, and many of his basic data were incorrect. It was Ernst Gottfried Fischer (1754–1831) who rationalized Richter's results and published the first table of equivalent weights; some of the values were surprisingly accurate.[37] It was Richter's work which led Berzelius to his atomic weight determinations.[38]

The next important figure on the scene was Martin Heinrich Klaproth (1743–1817), who inherited Valentin Rose's pharmacy in Berlin when Rose died four weeks after Klaproth started work there. He later married a niece of Marggraf and bought a laboratory with her dowry. He was a very accurate analyst, and very pragmatic in outlook. He discovered uranium, zirconium and cerium and named titanium, strontium and tellurium. Szabadváry has given an extensive list of Klaproth's contributions to analysis,[39] and pointed out that he was the first to give full procedural details for methods, and a truly quantitative outlook (he sought for the source of discrepancies from 100% for a total analysis), and found new elements and investigated the distribution of the elements in natural products, finding potassium in both vegetables and minerals, for example. He also originated alkaline fusion (with potassium hydroxide in a silver crucible, and used platinum for the sodium carbonate fusions developed by Marggraf), and went so far as to measure the loss of material from the mortar used for grinding samples and to apply a correction. He also developed the idea of ignition to constant weight.

At about this time the first books devoted to analysis began to appear, the first being by Johan Friedrich Göttling (1755–1809),[40] followed by that by Wilhelm August Lampadius (1772–1842), Professor at the Mining Academy,[41] who gave the first quality control tests for analytical reagents (including distilled water) and noted the green flame of alcohol containing boric acid. This particular series of books culminated in the work by Christian Heinrich Pfaff (1773–1852) who produced the first comprehensive handbook of analytical chemistry.[42] This was the first of the long series of German texts on analytical chemistry, which were pre-eminent in their field up to the first world war.

THE GOLDEN AGE

The nineteenth century saw the great flowering of analysis in Germany. To a large extent this was a consequence of the rise of the chemical industry and the realization that production and quality control could produce a profit. Scott[1] considers that much of the rise of the German chemical industry was due to Mohr's work on titrimetry. The German universities came to be regarded as the research centres of Europe, and for British and other graduates a research training in Germany was not unusual. During this period quantitative analysis was firmly established and new techniques were rapidly developed.

In gravimetric analysis, Heinrich Rose (1795–1864), who was a grandson of Valentin Rose and whose father was a pupil of Klaproth, made a number of advances.[43] He discovered niobium, was the first to use an acidic fusion for decomposition (with potassium bisulphate), and developed the crucible named after him and used for reduction of oxides to metals by ignition in a reducing atmosphere. He also produced a scheme of qualitative analysis based in part on the use of hydrogen sulphide. His "Handbuch der analytischen Chemie" was published in 1829, and was still used as a standard text (the 7th edition appeared in 1871) in the last quarter of the century. The book, though packed with information, and organized element by element, is practically devoid of references to the literature and is difficult to use. It was this difficulty, experienced by beginners, that led Carl Remigius Fresenius (1818–1897)[44] to develop his own scheme of qualitative analysis, based on his own needs as a student, and (at his professor's suggestion) to write his own text "Anleitung zur qualitativen chemischen Analysen" (1841), which ran to seven editions in 10 years, and had reached its 16th by the time of the author's death. He also established the Fresenius Institute in Wiesbaden, and founded the oldest purely analytical journal, *Zeitschrift für analytische Chemie*, which he edited until his death.

The stage was now set for the appearance of Mohr. Up to this time the home of titrimetric analysis was France, where most of the techniques and methods had been developed, and the few German research workers in the field had mainly studied the science in French laboratories. The advantages of the technique were fairly obvious, however, and once interest had been aroused, action followed.

Margueritte's permanganate titration of ferrous iron[45] had appeared in 1846, and was soon used in a number of indirect determinations, including the chromate titration developed by Schwarz.[46] When direct titration of chromate was developed by Schabus[47] and by Penny[48] (independently), the need for an external indicator led to criticism by Schwarz on the grounds of inaccuracy.[49]

Karl Leonhard Heinrich Schwartz (1820–1890)[50] studied titrimetry in France, and produced the first German textbook on the subject,[21] introducing the term "Massanalyse" into the language. Justus von Liebig (1803–1873)[51] developed the first complexometric titration[52] (cyanide with silver nitrate) in 1851, and was the first to use mercuric nitrate as a titrant[53] (in 1853). Robert Wilhelm Bunsen (1811–1899)[54] was also active in this field and developed the general technique of iodometry, describing some 18 determinations in a single paper.[55] He used sulphurous acid for titrating the iodine, and this reagent was used long after, although Schwarz introduced thiosulphate as titrant in the same year.[21] Bunsen is a typical example of the versatility of the great chemists of the time, with wide-ranging interests. His achievements, whether design of simple but extremely useful apparatus such as the Bunsen valve and the Bunsen burner, or more profound such as his work on spectroscopy, was always useful and superbly executed. He was famous for his practical skill and had no sympathy for hypothesis and theorizing. His dictum "Ein Chemiker der kein Physiker ist, ist gar nichts" sums up his opinion of how a chemist should be trained. He was kind-hearted, with a keen sense of humour, but would not have women students, especially Russian ones. He had to yield once, however, when on behalf of a countrywoman, the Russian mathematician Sonja Kowalewski interceded with him, having left at home the large floppy hat she habitually wore to hide "those marvellous eyes whose eloquence, when she wished it, none could resist".[56] It is also related that a certain student, bringing his attendance card to be signed, said "Behind the pillar, Herr Professor" when asked where he sat in lectures, and that Bunsen replied "So many of you do" but signed the card nevertheless.[57]

Amongst other techniques developed then and still in use, the stannous chloride/mercuric chloride method for reduction of ferric iron[58] [Friedrich Christian Kessler (1824–1896)][8] may be mentioned, and the Zimmermann–Reinhardt reagent[59] [Julius Clemens Zimmermann (1856–1885) and C. Reinhardt]. Jacob Volhard (1834–1910) is now remembered more for his argentometric back-titration method[60] (also discovered independently by Charpentier four years earlier[61]) than the determination of manganese[62] that is also named after him. Later in the century, Hans Heinrich Landolt (1831–1910) whose name is perpetuated in the Landolt reaction and the Landolt–Börnstein Tables, suggested gravimetric determinations by bromination of certain organic compounds,[63] and this was developed into a titrimetric method by Koppeschaar.[64] Hübl[65] developed the first method for iodine number determinations, but bromine numbers had been used much earlier[66] [August Wilhelm Knop (1817–1891)]. Lange was using ceric sulphate as titrant as early as 1861,[67] but the lack of redox indicators was a handicap.

Acid–base indicators had been discovered early on, of course, and Caspar Neumann (1683–1737) may be credited with realizing the possibility of end-point detection.

Krüger made the first use of a fluorescent indicator (fluorescein) but it was overshadowed by the rapid introduction of phenolphthalein (E. Luck),[70] Tropaeolin (M. Miller)[71] and Methyl Orange [Georg Lunge (1839–1923)].[72] Lunge is, of course, also well known for his work on gas analysis.

At this stage the great theorists began to emerge, and Wilhelm Ostwald (1853–1932) in "Die wissenschaftlichen Grundlagen der Analytischen Chemie" gave his theory of indicator action, which in turn led to Hans Wilhelm Friedenthal (1870–1943) developing colorimetric determination of hydrogen-ion concentration,[73] with the aid of buffers (suggested by the Hungarian chemist Szily).

Although the most exciting developments appeared in titrimetry, several workers were active in other fields. In organic analysis, for example, Johann Wolfgan Döbereiner (1780–1849), better known for his "triads", had designed a simple combustion apparatus,[74] and Justus von Liebig had developed his method for carbon and hydrogen determination,[75] which later greatly benefited from Bunsen's invention of his gas-burner.

The Dumas method for nitrogen was difficult to use until the nitrometer was invented; the first useful one was due to Schiff in 1868,[76] but meanwhile Franz Varrentrapp (1815–1877) and Heinrich Will (1812–1890) had produced their method[77] based on production of ammonia by ignition of the sample with barium hydroxide, which was modified by Péligot[10] and swept the field until it was superseded by the Kjeldahl method.

Even August Kekulé (1829–1896) ventured into analysis, and developed a method for halogens in organic compounds,[78] but it was not universally applicable, and Georg Ludwig Carius (1829–1875) developed his well-known sealed-tube method for determining sulphur as well as halogens.[79]

Physical methods

During this period of highly productive explor-

ation, physical methods of analysis also began to be developed. In some respects they were before their time, because although the principles were established, the requisite apparatus for their application could not be devised. Atomic-absorption spectrophotometry is perhaps the best known example.

Optical methods. In the 18th century the difference in flame colour caused by sodium and potassium had been noted by Marggraf,[80] and Johann Wilhelm Ritter (1776–1810) discovered ultraviolet radiation and noted its effect on silver chloride.[81] Josef Fraunhofer (1787–1826) rediscovered Wollaston's "black lines" and catalogued them[80] and laid the foundations of absorption spectrometry.[82] Julius Plücker (1801–1868) showed that the discharge spectrum was characteristic of a gas,[83] and Johann Wilhelm Hittorf (1824–1914) established the existence of line and band spectra.[84] The culmination of the early work was the development of spectrum analysis by Gustav Kirchhoff (1824–1887) and Bunsen[85] which almost at once resulted in the discovery of rubidium and caesium.[86] Kirchhoff also reported line-reversal.[87] Bunsen, who as already said is one of the outstanding analytical chemists of all time, was the inventor of many pieces of apparatus named after him[88] (including the water-pump,[89] the carbon–zinc battery[90] and the wax-spot photometer[91]), and besides working on spectrometry was also associated with iodometry,[55] gas analysis,[92] electrochemistry, and other topics. However, the early work was purely qualitative, and as late as 1910 Heinrich Kayser (1853–1940) held that quantitative spectrum analysis was impracticable,[93] only to be proved wrong by Walter Gerlach with his method of line-pairs.[94]

Colorimetry was developed empirically from about 1840, by Lampadius[95] and Carl Heine,[96] and the first colorimeter[97] was designed by Alexander Müller (1828–1906). The theoretical basis of spectrophotometry (the Lambert–Beer law) was laid by the work of Johann Heinrich Lambert (1728–1777) who recognized the relation between absorption and the number and size of the absorbing centres in unit volume,[98] and of August Beer (1825–1863) who established the relation between absorption and concentration.[99] (It should be noted that these relationships were also discovered independently by Bouguer and Bernard.[100]) It was Bunsen and Roscoe who introduced the idea of an absorption coefficient[101] and Bahr and Bunsen who first used absorption spectroscopy quantitatively.[102] The founder of modern spectrophotometry, however, was Carl Vierordt (1818–1884) who realized how the Lambert–Beer law and Bunsen–Roscoe absorption coefficient could be used, and published a table of absorbance–transmittance values.[103] The first comprehensive account was given in the book[104] by Gerhard Krüss (1859–1895), the founder of *Zeitschrift für anorganische Chemie.* The use of photo-cells for detection was initiated by Wilhelm Berg.[105] The firm of Carl Zeiss, Jena, is world-famous for its optical equipment.

Electrochemical methods. The hydrogen electrode was devised in 1893 by Max le Blanc[106] (1865–1943) and was used by Wilhelm Böttger (1871–1949) for the first potentiometric acid–base titration[107] in 1897. The first potentiometric titration of all, however, was in 1893 by Robert Behrend (1856–1926), who used a mercury electrode and mercury/mercurous nitrate electrode for titration of mercurous nitrate with potassium chloride, bromide or iodide[108] and a silver electrode and silver/silver nitrate reference electrode for titration of iodide with silver nitrate. The basis of the glass electrode was noted by M. Cremer,[109] and Fritz Haber (1868–1934), working with Klemensiewicz, observed that it should be possible to use a glass electrode instead of the hydrogen electrode.[110] The principle of "dead-stop" end-point detection seems to have been discovered by Ernst Salomon in 1897.[111] Harber, of course, is one of the greatest German chemists, and his ammonia process a lasting monument (Nobel Prize 1918).

Conductometric titration is based on the work of Friedrich Kohlrausch (1840–1910) on conductivity, and the Kohlrausch bridge[112] is still used (though in rather modified form). The first analytical application was by Friedrich Wilhelm Küster (1861–1917) and Max Grüters,[113] and the technique was later used extensively by Gerhart Jander (1892–1961).

Electrogravimetry may also be included in this section. C. Luckow can claim[114] to have discovered the method independently of Wolcott Gibbs. Alexander Classen (1843–1934) worked extensively on the technique, making numerous valuable contributions, including the first book,[115] which came to rank with the works of Fresenius and Mohr. Luckow also used the mercury cathode for electrolytic separations.[116]

Theory of analysis

Another rapid development in this period was analytical theory, and the publication of monographs (some of which have already been mentioned).

Ludwig Ferdinand Wilhelmy (1812–1864) may be regarded as founding kinetic methods by his work on the inversion of cane sugar, Rudolph Clausius (1822–1888) contributed to the development of thermodynamics (so essential for understanding analytical chemistry), and August Horstmann (1843–1929) made the first chemical applications of thermodynamics. Wilhelm Pfeffer (1845–1920) made a semi-permeable membrane and conducted the first osmotic pressure measurements, which later led to van't Hoff's theory.

Hittorf and Kohlrausch, with the work on ionic mobility, transport numbers and conductance, established many of the facts later used in the Arrhenius theory and explained by it. Arrhenius's theory also clarified various other aspects of the chemistry of electrolytes in solution and was later itself related by Ostwald to the law of mass action. Ostwald was the first of the great theorists of analytical chemistry, and his book on it has already been mentioned. His contributions to chemistry are much more extensive than

this, of course,[117] and his Nobel Prize in 1908 was well deserved. His systematic presentation of the physical chemical basis of analytical chemistry set the pattern for future generations of textbooks.

Curiously, Ostwald seems to have ignored the value of redox methods and the Nernst equation in analytical chemistry.[118] Walther Nernst (1864–1941), another Nobel Prize winner (1920), was in many ways as important a figure as Ostwald in chemistry in Germany.

The Nernst equation[119] is fundamental to redox chemistry, and nowadays to direct potentiometry, and in those contexts perhaps owes as much to Richard Peters.[120] The Nernst distribution law[121] has had equally far-reaching consequences in analytical practice and in technology. A fascinating biography of Nernst has been written by one of his pupils[122] and is equally interesting as an account of the scientific scene in Germany in the last hundred years.

Nernst was the subject of many anecdotes. One concerns his retirement, and his abandoning his herd of cows in favour of carp-rearing because the fish were in isothermal equilibrium with their environment, and Nernst did not see why he should pay to increase the heat of the atmosphere.[122, 123] Another refers to his dislike of "named" units, and his proposal (when the Hertz was decided on) that there should be a unit of flow, 1 litre/sec, to be called the Falstaff.[124] He also said that as the number of "discoverers" of the laws of thermodynamics decreased as the number of the law increased, and he was the sole discoverer of the third law, the fourth law would have no discoverers at all.

The early work on determination of hydrogen-ion concentration has already been mentioned, but the importance of pH in chemistry was first thoroughly realized by a biochemist, Leonor Michaelis (1875–1949). Michaelis also made a fundamental contribution to the theory of redox indicators and acid–base indicators.[125]

Organic reagents

The late 19th century was the great era of organic chemistry in Germany, and it is not surprising that the use of organic reagents in analysis was realized. Thus Peter Griess (1829–1888) used various amines as reagents for nitrite,[126, 127] and his method based on the coupling of sulphanilic acid with the diazotization product of α-naphthylamine,[127] in the form developed by Ilosvay[128] and now modified because of modern views on carcinogens, is still used. Otto Brunck (1866–1946) first used the organic complex of a metal ion as the final weighing form, with the α-nitroso-β-naphthol complex of cobalt in 1907.[129] Oskar Baudisch (1881–1950) introduced the use of cupferron in 1909.[130] Wolf Müller (1874–1941)[131] used benzidine for sulphate determination and Max Busch (1865–1941) introduced nitron as a reagent for nitrate.[132]

The correct temperature range for drying or igniting such precipitates is important, and the thermobalance has played a major part in this field. Some of the first experiments were by Nernst and Riesenfeld.[133]

Microanalysis

Edgar Hugo Reinisch (1808–1884) was an early worker in the use of microscopy as a means of identification of crystals obtained by evaporation, but considerably more work was done by Karl Haushofer (1839–1895),[134] who developed several new techniques, including micro-filtration. A major problem, of course, was provision of a sensitive balance, and again Nernst was first in the field, with a quartz fibre torsion balance.[135] The Kuhlmann and Bunge balances were developed shortly after, and achieved great renown; Sartorius balances were also famous. Pure reagents were also necessary and the firm of Kahlbaum introduced reagents of guaranteed purity in the late 19th century.

THE FALLOW YEARS

For various reasons (political, social, economic, the decline of the German chemical industry and the increasing investment in British and American chemical production) the years between 1914 and 1945 saw a somewhat less rapid and exciting advance in analytical chemistry in Germany. There was a period more of consolidation than of innovation, though certain developments must be recorded. Most analytical work was still classical in type, and instrumentation was developed only slowly. Nevertheless, there was an early interest in automation, especially in development of industrial control methods, which led to the surprise expressed by Belcher and Phillips at the extent of automation of organic microanalysis in German.[136]

In the optical methods Eugen Schweitzer (1905–1934) further developed[137] Gerlach's line-pair method,[94] and Günther Scheibe and Neuhäusser[138] brought in the use of the logarithmic sector. In flame photometry, Wolfgang Schuhknecht used simple coloured filters instead of a monochromator.[139]

In electrochemistry, H. Fritz developed electrography.[140] Radiochemistry was in its infancy, and Rudolf Ehrenberg was one of the pioneers of the use of radioactive reagents,[141] a field that is still fruitful. Erbacher and Philipp[142] introduced the use of radiotracers for examination of efficiency of separation.

In separation methods, Richard Kuhn, Nobel Prize winner in 1938, was active in chromatography of carotenoids,[143] A. Bahrdt used a zeolite column for ion-exchange,[144] and Gerhard Hesse laid the foundations of modern gas adsorption chromatography.[145]

Meanwhile, steady progress was being made in organic analysis. Walter Hempel (1851–1961), well known for his work on gas-analysis, had tried unsuccessfully to determine oxygen in organic compounds by combustion to carbon dioxide followed by reduc-

tion to carbon monoxide, and it was not until 1939 that Max Schütze solved the problem,[146] by pyrolysis in the presence of carbon in an inert atmosphere, the method being further developed by Wilhelm Zimmermann[147] and Josef Unterzaucher.[148] It was also Zimmermann's work on automation of organic analysis that partly inspired Duval's development of thermogravimetric methods. In qualitative analysis Hermann Staudinger (1902–1965; Nobel Prize 1953) investigated functional group reactions and classification of organic substances.

Work on organic reagents for inorganic analysis was also steadily developed during this period, notable typical contributions being the introduction of dithizone[149] by Hellmut Fischer in 1925, oxine by Friedrich Hahn and Karl Vieweg[150] and by Richard Berg[151] (who disputed priority) in 1927, and thionalide[151] (also by Berg) in 1935.

An equally far-reaching discovery was the development of the Karl Fischer reagent[153] in 1935. Around this time the first complexones were developed by I. G. Farbenindustrie, although they were then used only in industrial applications, their analytical use being discovered much later.

One interesting but little-known development was the use by Preuss of a carbon tube heated to 1600–1800° as an auxiliary atomization device in spectrography.[154] This is clearly a forerunner of the carbon tube techniques developed in the 1960s for atomic-absorption spectroscopy.

Analytical research in this period followed the general pattern of chemical research. Whereas in the early 19th century research was centred mainly in the universities, later on industrial research became more important. Indeed the first industrial research laboratory was established by Emmanuel Merck at Darmstadt in 1826. The BASF, Hoechst, and Bayer laboratories were developed later (in the 1860s and 1870s) and by 1910 industry employed more chemists than the universities did. The war, however, caused severe disruption, and the loss of international patent rights cost the German chemical industry its world supremacy. Inflation increased the erosion of research and development, but the chemical industry continued extensive research, and in 1925 I. G. Farbenindustrie A. G. was established and conducted a great deal of pioneering work. Politics entered the scene, however, and both basic and applied research was pursued haphazardly according to the dictates of the moment. There was also considerable loss of scientists by compulsory or "voluntary" removal from their posts, and between 1933 and 1939 the intake of science and technology students to the universities was more than halved, and a quarter of the total university staffs had been dismissed. German science was at a low ebb. Research continued, of course, in the schools developed by such deeply respected analysts as Wilhelm Geilmann (1891–1967), but political interference left a lasting mark. One of the few benefits was that Haber and Nernst, whose relationship had long been polite but unfriendly, finally became united when Nernst found the policy towards Jews unacceptable, offered Haber his hand, and asked if Haber could find him a post in his institute as he felt he could no longer work in his own. Haber, however, had himself just resigned as Director of the Institute for Physical and Electrochemistry at Berlin-Dahlem, for the same reason.

THE RESURGENCE

The post-war years need little description here—their history will be already well known to readers.

The second world war had further depleted Germany's scientific strength, few scientists being excused military service, but once the ravages of war had been repaired, German research effort entered a new phase, not so much innovatory in character, but with the main emphasis placed on consolidation and application of the new discoveries made elsewhere. The result has been a steady expansion of research, especially in the Max-Planck Institutes (worthy successors to the Kaiser Wilhelm Institutes) and an impressive body of published work.

It is difficult to compile a list of contemporary German contributions to knowledge without fear of making invidious distinctions, but there can be no doubt about the importance of the contributions of Rudolf Bock and Helmut Bode in solvent extraction chemistry, of Heinrich Kaiser and Hermann Specker in spectrography and detection limit criteria, Klaus Doerffel and Günter Gottschalk in statistics and information theory, Günter Tölg in ultratrace and ultramicroanalysis, Bruno Sansoni and Ewald Blasius in ion-exchange and electrophoresis, Kurt Laqua in laser methods, Siegfried Hofmann in surface analysis, Gerhard Ackermann (continuing the Freiberg mining academy tradition) in organic reagents, Gerhard Werner in kinetic methods, Wolfgang Merz in automation of organic analysis, Knut Bächmann in inorganic gas chromatography, Herbert Weisz in trace analysis, Rolf Neeb and Hans-Wolfgang Nürnberg in polarography or Dieter Klockow in environmental analysis, and these are but a few of the names well known in the literature of modern analytical chemistry. In addition, workers such as Fritz Umland have contributed to many fields of analysis. The most outstanding contributions are perhaps the Mössbauer effect and the development of Mössbauer spectroscopy, the Massmann furnace in atomic-absorption spectrophotometry, and Egon Stahl's work in thin-layer chromatography.

To sum up this necessarily brief survey, we can see that German resource and inventiveness has been instrumental in furthering the development of analytical chemistry from its earliest years right up to the present, more vigorously at some times than others, but never stopping completely. There is a long record of both innovation and development, and there has always been close co-operation between academic and industrial research and requirements, and a generally

sound appreciation of the importance of analytical chemistry. Many of the everyday tools of the analyst spring from German discoveries, and the world owes German science a considerable debt.

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RATIONALES UND IRRATIONALES ZUR FRAGE: WAS IST ANALYTISCHE CHEMIE?

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Zusammenfassung—Um die Stellung der Analytischen Chemie in der Wissenschaft klären zu können, werden einige philosophische Betrachtungen herangezogen und Kurzdefinitionen angeboten.

Folgt man Szabadváry in seiner Darstellung der Geschichte der Analytischen Chemie,[1] so war Friedrich Mohr für seine Zeitgenossen fürwahr kein einfacher Mensch weil er ein geistig äußerst beweglicher, vorausblickender und vielseitiger Wissenschaftler war. Er hat mehr in Bewegung gebracht als es seine, uns überlieferten Ausführungen zur Maßanalyse bisher vermuten lassen. Seine Einstellung zur Energieerhaltung z.B. war neu, enthielt für die damalige Zeit noch Irrationales war somit unbequem und wurde daher vielfach abgelehnt. Eine Situation die in der Wissenschaft oft angetroffen wird.

Die letzten 100 Jahre haben erfreuliche und erstaunliche Fortschritte in und mit der analytischen Chemie gebracht, sind im tiefen Wesen aber immer stärker in das, wenn auch in dem hochstehenden so doch im wesentlichen "handwerklichen" Milieu verblieben. Dies führte u.a. dazu, daß heute über das "Dienstmädchendasein" der Analytischen Chemie gejammert wird. Kein geringerer als Ostwald[2] hat schon 1917 auf Grund und Ursache dieses Zustandes hingewiesen. Wörtlich schreibt er in seinem Vorwort zur 1. bis 6. Auflage der "Grundlagen der Analytischen Chemie": "... Dementsprechend nimmt neben den anderen Gebieten unserer Wissenschaft die Analytische Chemie die untergeordnete Stelle einer—allerdings unentbehrlichen—Dienstmagd ein. Während sonst überall die lebhafteste Tätigkeit um die theoretische Gestaltung des wissenschaftlichen Materials zu erkennen ist, und die hierher gehörigen Fragen die Gemüter stets weit stärker erhitzen, als die rein experimentellen Probleme, nimmt die analytische Chemie mit den ältesten, überall sonst abgelegten theoretischen Wendungen und Gewändern vorlieb und sieht kein Arg darin, ihre Ergebnisse in einer Form darzustellen deren Modus oder Mode seit fünfzig Jahren als abgetan gegolten hat. Denn noch heute findet man es zulässig, nach dem Schema des elektrochemischen Dualismus von 1820 beispielsweise als Bestandteile des Kaliumsulfats K_2O und SO_3 anzuführen; und die Sache wird nicht besser dadurch, daß man daneben Chlor als solches in Rechnung bringt, und sein "Sauerstoffäquivalent" von der Gesamtmenge in Abzug bringen muß".... "In den drei Jahren, die bisher zur Ausgabe der zweiten Auflage verflossen sind, hat sich an dem allgemeinen Zustand der analytischen Chemie nicht viel geändert, insbesondere bin ich nicht gewahr geworden, daß die auch in diesem Zeitraume zahlreich genug erschienenen neuen oder wieder aufgelegten Lehrbücher der analytischen Chemie der neueren Ideen in den Kreis der gebräuchlichen alten Darstellungsweise, die doch schon längst unzulänglich geworden ist, hätten erkennen lassen."

Ein wesentlicher Grund dieses auch im 20 Jahrhundert noch anhaltenden Zustandes liegt in der Tatsache, daß sich die Analytiker nicht verständlich genug artikulieren konnten und immer wieder vergessen, daß das zur Diskussion stehende "Ding", das "Probegut" in zwei Erscheinungsformen auftritt, als Materie *und* als Form. Der Stoff hat sein komplementäres "*alter ego*" in der Form. Meines Erachtens hat der Mangel an alteregoistischen Betrachtungen dazu geführt, daß man meist bei der Bestimmung der Materie verblieb, der Form fast keine Beachtung schenkte.

Seit einiger Zeit ist aber weltweit ein Suchen nach anderen und scheinbar "neuen" Grundlagen als nur die Gesetze der Chemie im Gange. Man wird aber im Finden nicht sehr erfolgreich sein, wenn wir uns nicht entschließen, Analysis in den philosophischen Wurzeln zu fassen.

PHILOSOPHIE UND ANALYTISCHE CHEMIE: (EINE EINFÜHRUNG)

Allgemeines und Grundsätzliches

Wie das Studium der Mathematik (oder Physik) kann auch das Studium der Analytischen Chemie in zwei verschiedenen Formen durchgeführt werden. Erstens pragmatisch—konstruktiv, Schritt für Schritt, vom Nachweis zur Bestimmung, von der Demonstration zur handwerklichen Perfektion und zweitens logisch–analytisch, vom Problem als Black-Box bis zur Abstraktion des Problems in Entitäten. Der erste Weg ist der bisher (schulisch) erprobte und begangene. Er soll und darf im Sinne unserer Gesellschaft

nicht verlassen werden, sondern muß die notwendigen Ergänzungen erfahren. Der zweite Weg aber führt uns in die Gebiete wo sich größere Zusammenhänge zu erkennen geben; z.B. die Unauflöslichkeit der Komplementarität von Form und Materie und bedarf sicherlich der Einbeziehung von Momenten aus dem ersten Weg.

Es war schon immer die Aufgabe und der Zweck der analytischen Philosophie aus Prämissen über geeignete Syllogismen Schlüsse (Konsequenzen) aus einem System zu ziehen. Die Anwendung der analytischen Philosophie auf materiellem System, wie z.B. in der Analytischen Chemie immer notwendig ist, führt erst zur Aufklärung der Art und Wirkungsweise der das System aufbauenden Systemelemente, wobei es vorderhand sekundär ist ob wir diese Entitäten, Monaden, oder sonstwie bezeichnen, wenn wir sie nur eindeutig definieren.

Um die Zusammenhänge etwas klarer aufzuzeigen sollen einige Worte über Philosophie und Wissenschaft verloren werden.

Waismann,[3] zitiert bei der Behandlung der Frage: "Was ist Philosophie", Wittgenstein wie folgt: "Philosophie ist keine der Naturwissenschaften. Der Zweck der Philosophie ist die logische Klärung der Gedanken. Die Philosophie ist keine Lehre sondern eine Tätigkeit. Das Resultat der Philosophie sind nicht philosophische Sätze, sondern das Klarwerden von Sätzen. Die Philosophie soll die Gedanken, die sonst trübe und verschwommen sind, klar machen und scharf abgrenzen". Auch Kant wollte nie Philosophie sondern Philosophieren lehren. Sehr deutlich beschreibt auch Huxley[4] die Situation: "Philosophie wird heute von vielen Philosophen als Analyse verstanden, wobei dem Analytiker die Aufgabe zufällt Zweideutigkeiten aufzuklären und die Bedeutungen von Behauptungen klar zu definieren". Auch Wissenschaft ist keine Lehre, man betreibt sie. Von Weizsäcker[5] sagt, anknüpfend an eine Anekdote, in der falsche Messungen eine Rolle spielen: "... Das heißt, Wissenschaft ist leichter zu betreiben als zu verstehen". Dies gilt selbstverständlich auch für die Analytische Chemie. Auch sie ist wesentlich leichter (handwerklich) zu betreiben als mit ihr wissenschaftlich umzugehen, weil dazu auch Logik und Hermeneutik notwendig sind.

Sicher ist, daß Philosophie und Wissenschaft eines gemeinsam haben, die Beweisnotwendigkeit. Die Erbringung des Beweises, die Beweisführung erfolgt über den Prozeß des Argumentierens. Die logische Verknüpfung zweier, Subjekt und Prädikat erhaltene Prämissen ergeben, je nach Syllogismus, als Beweis (Konsequenz) richtige (wahre) Aussagen. Wenn die Prämissen richtig (wahr) sind so muß auch die Aussage (wahr) richtig sein. Andererseits kann aber trotz richtiger Beweisführung (Argumentation, Analyse) die Aussage falsch sein oder sich aufgrund neuer Erkenntnisse als falsch erweisen. Dies trifft in der Naturwissenschaft sogar relativ häufig zu. Auch kann ein Beweis trotz einer falschen Prämisse richtig sein. Z.B. nach Russell[6] "Kein Säugetier kann fliegen, alle Schweine sind Säugetiere, also kann kein Schwein fliegen". Der Schluß ist wahr obwohl die erste Prämisse falsch ist! (Fledermäuse können fliegen).

Seit über 2000 Jahren spielen Syllogismen (syl = syn = zusammen; logos = Wort, Satz, Gesetz *etc.*) eine entscheidende Rolle im menschlichen Fortschrittsstreben und sind weder aus der Philosophie noch aus Wissenschaft und Technik entfernbar, wo sie sowohl als einfache (kategorische, hypothetische oder disjunktive) Syllogismen als auch in Form von Peirce- und Shefferfunktionen bis in die Schaltungen von Computer hineinreichen.

Philosophie und Wissenschaften verlangen aber auch zwingend Logik und Hermeneutik, also Denken und Verstehen. Während Logik nicht nur die Fähigkeit, folgerichtig zu denken, ist, sondern auch die Lehre von den formalen Beziehungen zwischen Denkinhalten und deren Beobachtungen, ist Hermeneutik die Kunst oder die Fähigkeit richtig zu verstehen. Heisenberg,[7] z.B., schreibt in seinem Buch: "Der Teil und das Ganze". "... Die Positivisten würden wohl sagen, daß Verstehen gleichbedeutend sei mit Vorausrechnen-Können. Wenn man nur ganz spezielle Ereignisse vorausrechnen kann, so hat man nur einen kleinen Ausschnitt verstanden; wenn man viele Ereignisse vorausrechnen kann, hat man weitere Bereiche verstanden. Es gibt eine kontinuierliche Skala zwischen Ganz-wenig-Verstehen und Fast-alles-Verstehen, aber es gibt keinen qualitativen Unterschied zwischen Vorausrechenen—Können—und Verstehen".

Deutlich zeigt er am Beispiel des Flugzeuges am Himmel den bestehenden Unterschied auf. Wir können die Flugbahn vorausberechnen; verstehen, d.h. warum gerade diese Bahn gewählt wurde, können wir sie nur im Gespräch mit dem "Piloten". Auch wir "verstehen" Resultate nur dann, wenn wir dem Dialog zwischen Probe und Reagenz folgen können. Genauso wie im menschlichen Leben wir nur dann gut informiert sind wenn wir die Originalsprache in der eine Information ausgegeben wurde verstehen, genauso verhält es in der Wissenschaft mit den Metasprachen.

Diese Sprachen mit ihren Details in Bezug auf organische und anorganische "Wesen" müssen wir erlernen und verstehen.

Ist Analysis in der Philosophie (nach Kant) in Form der logischen Analyse der Prozeß der klaren und expliziten Statuierung von Gedanken und Dingen, die "im Konzept", in der Idee (des Postulates) bereits vorhanden sind, so bedeutet das Prädikat "analytisch", z.B. zu Lehrsätzen (Theorem) oder Wissenschaftzweigen, daß diesen durch die Auflösung (in Form von Definition, Interpretation, Einbeziehung der Mathematik *etc.*) ein hoher philosophischer Wahrheitsgehalt oder eine gesicherte Darstellung zukommt. Viele Philosophen vertreten den Standpunkt, daß Philosophie per se dauerndes Weiterfragen, dauernde Analyse ist.

Analysis in der Mathematik ist eines ihrer Haupt-

gebiete, (ebenso wie Geometrie, Topologie, Algebra und Arithmetik) und wird ihrerseits je nach Schule in unterschiedlich viele Untergebiete geteilt.

Für das Bild der heutigen Naturwissenschaften hat Analysis z.B. in Verbindung mit Physik und Chemie, die Fourier-Serien oder die mathematische Wahrscheinlichkeit in der Thermodynamik, eine entscheidende Role. Die analytische Geometrie z.B. als weiterer Zweig der Mathematik, ist die reproduzierbare und sichere Darstellung von Punkten im Raum mit Hilfe von Koordinaten und spielt in der Analytischen Chemie z.B. bei der stereometrischen Analyse sowie in der Konformationsanalyse eine ebenso große Rolle, wie die statistische Linear- und Flächenanalyse. Auch ohne, jetzt schon abstrahierend eine Definition für Analytische Chemie zu geben, wird klar, daß sie ihre Wurzeln in der Logik haben muß und die Frage: was ist Analytische Chemie, nur in diesem Kontext beantwortet werden kann.

Analytische Schlüsse (Syllogismen)

Der, in seinen Ursprüngen auf die eleatische Schule Parmenides zurückzuführende aristotelische Kanon z.B. legt folgendes fest:

1. Satz der Identität: Was ist, ist (Parmenides).
2. Satz vom Widerspruch: Nichts kann sein, und nicht sein.
3. Satz vom ausgeschlossenen Dritten: Jedes muß sein, oder nicht sein.

Vergleicht man dazu die ersten fünf Hauptsätze aus Wittgensteins "Tractatus logico-philosophierens"[8] so fühlt man sehr wohl die zeitgemäße Analogie, aber doch auch, im Hinblick auf seinen Lehrer Bertrand Russell,[9] ein gewisses Unbefriedigtsein. Hier ist aber auch die Spannweite und fast zeitlose Gültigkeit von mehr als 2000 Jahren alten philosophischen Grundsätzen am deutlichsten in den Syllogismen sichtbar werdend, zu erkennen. Wenn auch z.B. der Frege-Syllogismus umständlich erscheint, wird er nicht nur von Russell[9] verteidigt, sondern kann da er zwingend die Formulierung von Schlüssen verlangt, zur Heranbildung urteilsfähiger Analytiker von Nutzen sein.

Die zehn "aristotelischen" Kategorien—als Vorläufer der Definition und der Abgrenzungen in der heutigen Systemtheorie—hatten etwa diese Reihenfolge und beispielhafte Bedeutung:

1. Substanz:	Mensch	oder	Probe
2. Qualitität:	Mann		Eisen
3. Quantität:	Körpergröße		100 kg
4. Relation:	Krieger		Brückenteil
5. Ort:	Athen		Wien
6. Zeit:	Mittag		Morgen
7. Zustand:	schwitzend		rostig
8. Tätigkeit:	Schwert haltend		Verkehr tragend
9. Lage:	Stoa		Donauufer
10. Haltung:	rastend		gebrochen

Descartes (siehe Huxley[4]) hat bereits zum wissenschaftlichen Forschen vier Regeln zur Logik aufgestellt, die auch immer bei analytischen Arbeiten eingehalten werden müssen und in der PAMS-Technik[10] klar zum Ausdruck kommen.

1. Nur klare und genau definierte Ideen zu akzeptieren (Problemstellung).
2. Alle Probleme in so viele Teile wie möglich zu zergliedern (Schaffung von Systemelementen und Abgrenzungen).
3. Mit den einfachsten Problemen zu beginnen und zu den umfassenderen vorstoßen (Grundzüge der heutigen Systemtheorie).
4. Kein Teilproblem darf ausgelassen, alle müssen aufgezählt und eingegliedert werden (Vorläufer der heutigen Modellerstellung und Simulation).

In der traditionellen Logik bezeichnet man mit Syllogismus "Satzanordnungen" wobei aus zwei kategorischen Sätzen (hypothetischen, disjunktiven) als Prämissen ein wahrer Schluß gefolgert wird. Die Wahrheit des Schlußsatzes (Konsequenz) setzt die Wahrheit der Prämisse voraus. Die Logik kann aber "die" Wahrheit nicht erbringen, sie kann nur die Richtigkeit der gezogenen Schlüsse aufzeigen.

Ausgehend von der aristotelischen Lehre verfügt die heute auch noch gültige Logik über: 4 Figuren die zusammen mit 4 Quantoren (je 2 für die Qualität = bejahend *a* bzw. *i* oder verneinend *e* bzw. *o*; affirmo bzw. nego und 2 für die Quantität (allgemein = *a* bzw. *e* oder partikulär *i* bzw. *o*) über 16 Arten der Schlußurteil die auf 64 verschiedene Weisen gezogen werden können aber nur 19 gültige Schlüsse zulassen.

Der grundsätzliche Beweisführungsvorgang beruht auf zwei Subjekt–Prädikat Prämissen die einen Begriff gemeinsam haben. Der gemeinsame Begriff der Oberprämisse (des Obersatzes) und der Unterprämisse (des Untersatzes) verschwindet im Schlußsatz (der Conclusio).

Nach der Euler'schen Darstellung sieht z.B. für die Logik-Figur "Barbara und "Celarent" wie folgt aus: [bei Abb. 1 und 2 P ist das Prädikat des Obersatzes (obere Prämisse), S ist das Subjekt des Untersatzes (untere Prämisse), M ist dar Mittelbegriff].
Einfaches Beispiel für "Barbara" ist das folgende:

Sulfide (M) enthalten Schwefel (P)
Pyrit (S) ist ein Sulfid (M)
Pyrit (S) enthält also Schwefel (P)

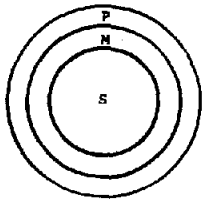

Abb. 1. M ist P, S ist M, S ist P.

Frege (siehe Russell[9]) hat u.a. auch gezeigt, daß Logik und Mathematik verschmolzen werden kann und entwickelte ein symbolisches System der logischen Folge.

Sein Symbol $\vdash$ für "wahr ist" zusammen mit den anderen Zeichen geben den 4 logischen Grundfiguren folgendes Aussehen.

1. $\vdash M f_1 P \wedge S f_2 M \rightarrow f_3 P$
2. $\vdash P f_1 M \wedge S f_2 M \rightarrow S f_3 P$
3. $\vdash M f_1 P \wedge M f_2 S \rightarrow S f_3 P$
4. $\vdash P f_1 M \wedge M f_2 S \rightarrow S f_3 P$

Wenn für "f" einer der Quantoren eingesetzt wird so ist der Syllogismus für:

Kein schwerlösliches Sulfid (M) gibt einen Chloridniederschlag (P).
Kupferionen (S) bilden schwerlösliche Sulfide (M).
Kupferionen (S) geben kr'n schwerlösliches Chlorid (P).

nach Frege:

$$\vdash MeP \wedge SiM \rightarrow SiP$$

M = Mittelbegriff = "kein schwerlösliches Sulfid" = allgemein verneinend daher "*e*".
S = Subjektbegriff = "Kupferionen" = partikulär, bejahend daher "*i*".
P = Prädikatbegriff = "Chlorid...".

Die Grundlage der logischen Beweisführung (der Analyse) also ist der gedankliche Zusammenhang (oder besser gesagt die Schaffung gedanklich richtiger Zusammenhänge) zwischen den zu beweisenden Satz und den Beweisgründen aus denen er abgeleitet werden kann.

Das folgende Beispiel zeigt die Aufstellung eines traditionellen kategorischen Syllogismus im Bereich der qualitativen Analyse: "Das Filtrat einer Aufschlämmung von AgBr in Wasser gibt mit Chloridionen ($[Cl^-] < 10^{-5}M$) keinen Niederschlag".

Die Abb. 2 zeigt die entsprechende Logik-Figur und ist die Darstellung für "Celarent".

Nach Frege sieht dies etwa so aus:

1. $\vdash [Ag^+]$ aus AgBr + $Cl^- \rightarrow 0$
2. Prämissen: $\vdash L_pAgCl \approx 10^{-10}$ und $[Ag^+] \approx 10^{-5}$
   $\vdash L_pAgBr \approx 10^{-14}$ und $[Ag^+] \approx 10^{-7}$
3. Syllogismus: $\underbrace{[Ag^+] < 10^{-5}M}_{(M)}$

$\underbrace{\text{geben keinen Chloridniederschlag}}_{(P)}$ $[Cl^- < 10^{-5}M]$

$\underbrace{[Ag^+] \text{ aus AgBr}}_{(S)}$ $\underbrace{ist \sim 10^{-7}M \text{ also}}_{(M)} < 10^{-5}M$

Daher gibt die Aufschlämmung keinen Niederschlag
(S) (P)

oder nach Frege

$$\vdash MeP \wedge SiM \rightarrow SiP$$

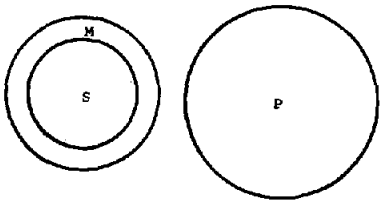

Abb. 2. M ist nicht P, S ist M, also S ist nicht P.

Wenn auch noch heute die auf Deduktion aufgebauten traditionellen Syllogismen bei der Analyse in Verwendung sind, so muß man doch feststellen, daß induktive Rückschlüsse, besonders in der Forschung große Bedeutung gewinnen. Dies auch deshalb weil es eine gültige Hypothese ist, daß Aufbau und Geschehen in der Wirklichkeit der Natur auf feste Ordnungen und Gesetzlichkeiten beruhen die in eine Stetigkeit der Weltevolution einmünden. In diesem Sinne sind induktive Schlüsse immer Wahrscheinlichkeitsschlüsse die auch Analogien einschließen.

Ein hypothetischer Syllogismus für den naturwissenschaftlichen Wahrheitsbegriff kann z.B. wie folgt lauten: "Wenn in einem rechtwinkeligen Koordinatensystem die Achsenabschnitte auf der zur Theorie (Berechnung) gehörenden Achse gleich groß sind wie jene zur Praxis (Bestimmung) gehörenden, dann dürfen wir das Ergebnis als wahr betrachten". Das heißt also "Wahrheit" ist: "tg $\alpha = 1$". Der einfachste Syllogismus hierzu ist nachfolgend beschrieben und bereitet jedem Analytiker diebische Freude.

1. Prämisse: $\frac{X_i}{Y_i} = 1$
2. Prämisse: $tg\alpha = \frac{X_i}{Y_i}$

Conclusio: $tg\alpha = 45° = 1$

Wenn man $\frac{X_i}{Y_i}$ als Mittelglied des Syllogismus betrachtet, "= 1" als Prädikat und "tgα" als Subjekt so ergibt sich daraus folgender Satz: $\vdash MaP \wedge SiM \rightarrow SiP$ der den Frege-Syllogismus zum obigen vollausgeschriebenen Satz darstellt.

Immer mehr werden auf Venn-Diagramme—oft ohne Einhaltung der Regeln der Logik—zur Aufhellung von Zusammenhängen in und mit der Analytischen Chemie verwendet. Hier sollen noch keine diesbezüglichen oder zur Boole'schen Symbolik notwendigen Ausführungen gebracht, und das Auslangen mit der traditionellen Logik gefunden werden. Damit können wir auch noch die dualistische, komplementäre, alteregoistische richtige Aussage: "Die Probe ist Materie und Form" so beweisen;

1. Satz: "Die Probe ist Materie"
2. Satz: "Die Probe ist Form"
Schluß: "Die Probe ist Materie und Form"

Hier gibt es keine Ober- und Unterprämisse und kein Mittelglied, ebensowenig wie im Satz: "Das

Tabelle 1.

Logos	Idee	Gedanke	Theorie
Kreation	Erzeugung	Herstellung	Synthese
Utilisation	Gebrauch	Nutznießung	Praxis
Description	Abbildung	Abbildung	Analyse

Licht ist Welle und Korpuskel" und auch hier würden sich die Venn-Kreise nahezu kongruent decken.

Diese Aussage über die Probe hat aber grundsätzliche Bedeutung für die moderne Analytische Chemie da jede Formänderung (insbesondere im Aggregatzustand) zu Informationsverlust führen muß. In weiterer Konsequenz führt dies, wenn die physikalisch-chemische Quantifizierung der Information möglich ist, zu ganz neuen Betrachtungen und Verwertungen von analytischen Signalen und Analysendaten. Ansätze dazu sind im Gange.

ZUM WESEN DER ANALTYISCHEN CHEMIE

Im letzten Teil seines Buches: "Die Einheit der Natur" beschäftigt sich von Weizsäcker[5] mit der klassischen Philosophie und bringt einleitend zu seinen Abhandlungen über "Parmenides und die Graugans" unter Hinweis auf Ideenhypothese von Platon und bei spezieller Verwendung zweier Beispiele (Lagerstatt und Zaumzeug) die Tatsache, daß jedes Ding in drei Stufen auftritt und zwar: Idee, Herstellung und Abbildung. Wenn man aber den Beispielen konsequent folgt, so fehlt in jedem Beispiel immer ein (wesentlicher) Begriffsbestandteil, bei dem Lagerstatt-Beispiel deren Gebrauch und bei dem Zaumzeug-Beispiel die Idee. Das heißt also, wir haben nach der Vierteilung zu suchen, wobei als Leitmotiv folgendes gelten kann: Aus welchen Gründen auch immer, zuerst ist (war) die *Idee*, dann deren Verwirklichung, d.h. *Herstellung*, dann der *Gebrauch* und schließlich die *Abbildung*. Überspannt man den ganzen Bogen von Platons "Politeia" bis Wittgensteins "Abbildungstheorie", so kann man geneigt sein, in Abwendung regulärer, geometrischer Körper, Tetreader zu bauen, um Platons Schönheitsideal vom verbundenen Elementardreieck nahezukommen und doch die vier vorher genannten Grundbegriffe wie Tabelle 1 und Abbildung 3 zeigen, untergebracht zu haben.[10] Außer der ersten Zeile können innerhalb dieser Tabelle die anderen vertauscht werden.

Demnach also ist Analyse immer eine Beschreibung, eine Abbildung, des nach einer Idee (Theorie) hergestellten Gutes im weitesten Sinne. Dies stimmt auch, denn zur Beschreibung muß der "Gegenstand" zerlegt werden. Je feiner die Zerlegung vor sich gehen kann, umso genauer ist seine Description.

Auch jede Wissenschaft begründet letzlich ihr "Dasein" auf vier Säulen, nämlich:

1. Theorie
2. Analyse
3. Synthese
4. Praxis

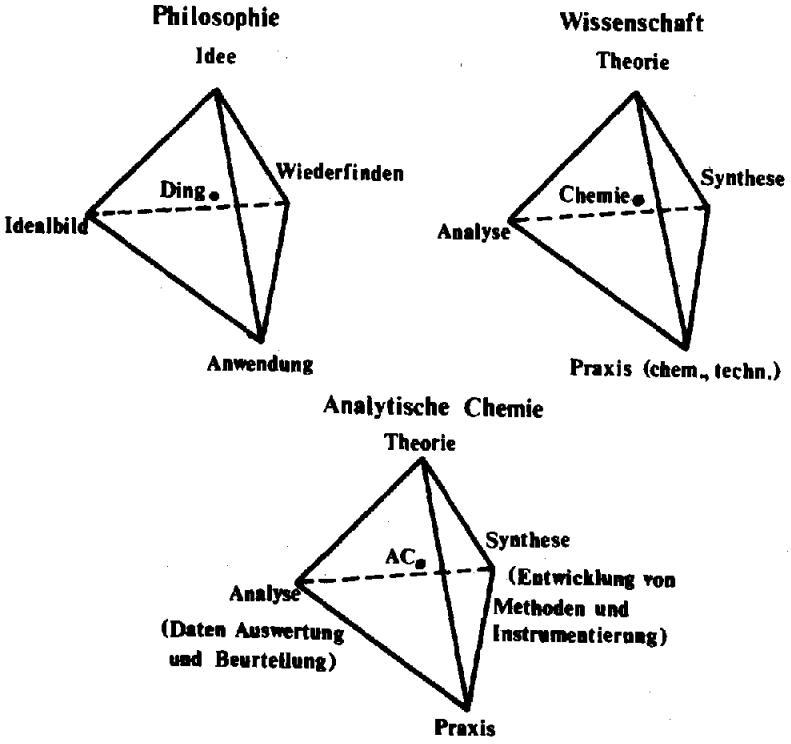

Abb. 3.

Tabelle 2.

Term	Umgang	Wissenschaft
Theorie	Gedankengang, Idee, Hypothese, Gegensatz zu Praxis. Bestätigte oder nicht bestätigte Spekulation.	Systematische, logische Anordnung einer Reihe von Propositionen, Postulaten usw. die zu einem Wissenschaftszweig gehören, aber durch das Experiment noch nicht bestätigt sein müssen.
Synthese	Gegensatz zu Analyse, Zusammenfügung getrennter Teile zu einer (neuen) Form. Erzeugung von Dingen.	Logische Kombination von getrennten Elementen zum Ganzen Im Sinne der Philosophie ist Synthese die Bildung eines Urteils über einen Gegenstand, wobei etwas neues ausgesagt wird, das nicht aus seinem Begriff folgt.
Analyse	Gegensatz zu Synthese, Auflösung eines Ganzen in Teile und dessen Beschreibung.	Logische Zergliederung in sinnvolle Entitäten und Auffindung logischer Funktionen und Reaktionen.
Praxis	Übung, Anwendung, Arbeitsstätte.	Erfolgreicher Umgang (Anwendung, Verwendung) von Theorie, Analyse und Synthese. "Es gibt nichts besseres als den praktischen Umgang mit Theorien!"

Diese Worte können ihrem Sinn und ihrer Bedeutung nach wie in Tabelle 2 zusammengefaßt, definiert werden.

Wenn man die Definition für die Begriffe der letzten Spalte der Tabelle 2 zuläßt and die entsprechende Terme in ein Tetreader einschreibt, so erhält man eine symbolische, ethische "*entelichea*" jeglicher Wissenschaft, jeglichen Problems und kann eine logische Abbildung der Vierbedingtheit unseres Seins und unserer Umwelt geben.

Analyse und Synthese sind bei der Praxis der Verifizierung von Theorien nahezu untrennbar miteinander verknüpft, denn anders können weder deduktive Urteile (d.h. Urteile vom Ganzen zum Teil oder vom Allgemeinen zum Besonderen) gefunden noch bestätigt werden. Dies gilt auch für materielle Dinge, hier geht es aber um richtige Zuordnung von Signalen bzw. Analysendaten. Dies ist analytische Synthese; ein ständiger Vergleich der Analysendaten der relevanten Probe mit dem Gesamtverhalten des Untersuchungsgutes. Jedesmal verringert sich der Informationsmangel zwischen Probe und Kollektiv. Dieser Vorgang hat so oft vor sich zu gehen bis eine Übereinstimmung von *rei et intellectus* (oder was wir dafür halten) erreicht ist. Bildhaft dargestellt erhalten wir dann eine Spirale die in die Spitze (die Wahrheit) eines Kegels einmündet, wobei das Wechselspiel zwischen Induktion und Deduktion sehr klar zum Ausdruck kommt.[11]

Die Strategie der Fragestellung (Methodenauswahl) und die spezifische Abfragung (Analysendurchführung) ist ein wesentliches Kennzeichen jeglicher Analyse und bedarf der Lehre in Theorie und Praxis. Erst wenn wir uns wieder bewußt werden, daß Wissen nur aus dem kognitiven Verhaltensschema gewonnen werden kann und wenn wir eine Brücke zwischen Philosophie und Informationstheorie bauen werden wir die komplexen und komplizierten Fragen unserer Zeit bewältigen.

Die Analogien zwischen menschlicher und maschineller Wissensbildung bestehen hierin, daß sowohl zur subjektiven Wahrnehmung als auch zum Messen des objektiven physikalischen Signal eine Änderung des jeweiligen "Grundstandes" erforderlich ist. Weiters, daß sich durch Assoziation, durch Aneinanderreihung von Wahrnehmungen, erst die Erfahrungen und das Lernen matritzenhaft erfassenlassen, ebenso wie die Nachricht im physikalischen Sinne die sinnvolle Aneinanderreihung von Signalen ist. Und schließlich, daß Wissen der logische Einbau von Assoziation ist, ebenso wie die logische Assoziation von Nachrichten erst die echte Information darstellt, erfaßbar durch die Decodierung von Signalen und Nachrichten.

Die Analyse ist somit aber auch *eine* Art der Verwirklichung der Wahrheitsdefinition, wie sie von Weizsäcker wiedergibt,[5] das Wegsuchen von Handlungensetzen, zum Auffinden der Übereinstimmung von Sache und Verstand.

Wie dies bewerkstelligt wird, welcher Syllogismus zur Anwendung kommt, bzw. kommen muß, hängt von der Fragestellung ab. Daher muß auch die reine Black-Box Philosophie mit Hilfe der System-, und Informationstheorie aufgehellt werden. Eine Grundlage dazu ist aber die Definition und rationale Zerlegung des gewählten oder vorgegebenen Problems. Wie die Zerlegung vor sich geht, ob und wo ein Rückschluß stattfindet, hängt vom Zweck, von der Fragestellung sowie von den praktischen Durchforschungsmöglichkeiten ab.

Eine ganz besondere Rolle spielen Metasprachen in Verbindung mit der Informations-, und Graphentheorie bei der Optimierung von analytischen Verfahren. Die Abfragung irgendeines ideellen oder materiellen Dinges im Sinne der analytischen Philosophie, wie sich von Parmenides ausging, ist im System einsichtiger Regeln der operativen Logik eingebettet. In der griechischen Philosophie bedeutet z.B. "*Nous*" soviel wie der "gottähnliche Geist", der die Welt gestaltet oder "formt" d.h. also, der Geist oder in weiterer Abstraktion der "*Logos*", der der "nackten" Materie die "sichtbare" Form gibt. In diesem Sinne

finden wir praktisch einen zwangslosen Übergang zur (ebenfalls) materie- und energielosen "Information", denn "*informare*" bedeutet nicht mehr und nicht weniger als "Form einprägen".

Die Behauptung, daß konkret die Form ohne Materie ebensowenig vorkommt wie umgekehrt, muß als feste Tatsache hingenommen werden, um materielle Dinge analysieren, d.h. körperlich und geistig "begreifen" zu können. Es geht also einfach darum ein Teilstück unserer Umwelt, eines zusammengewachsenen "*Synholons*", wie es von von Weizsäcker bezeichnet wird, bzw. das "*Morphem*" der Griechen, die kleinste bedeutungsvoll geformte Einheit, die Monade von Gottfried von Leibniz, auf seine *Form und Materie* zu prüfen, zu analysieren, um uns zu informieren. Aber bereits im Wort "Information" ist ja—form—bereits enthalten. "Formen, "gestalten", "prägen" beinhaltet sowohl das platonische "*Eidos*" (Zeichenform) als auch die aristotelische Form vom Idealkörper usw. Information über unsere (materielle) Welt kann nur aus dem Dualismus Materie–Form erhalten und verstanden werden, wenn wir "richtig" analysieren. Das heißt aber, für den Analytiker einfacher ausgedrückt: Das zu untersuchende, unbekannte Gut, die Probe, das Problem, besteht aus Materie und Information und wir müssen Mittel und Wege finden, beide für uns zugänglich und verständlich zu machen, um das Ganze zu "erfassen" und den Satz: "das Ganze ist mehr als die Summe seiner Teile" zu begreifen.

Hier scheint es angezeigt auf Ursprung und Bedeutung des Wortes "Probe" hinzuweisen. In der lateinischen Sprache heißt *probare* prüfen, testen, also auch analysieren und die Probe ist das vorliegende oder vorgelegte Gut. Problem kommt vom griechischen *proballein* (lat. *problema*) und heißt soviel wie "vorlegen" oder "vorwerfen", als etwas "Vorliegendes" behandeln. Ein Problem analysieren heißt auch dieses lösen und aufklären. In unserem Sinne ist die Probe das sichtbare Symbol einer mehr oder minder großen Gesamtheit und als solches das wichtigste und wertvollste Glied im System "Analytische Chemie".

Sehr interessant ist aber auch die Tatsache, daß wir in der Analytischen Chemie immer vom Reagenz und von der Reaktion sprechen und fast nie die Worte Agens oder Aktion gebrauchen. So hat es den Anschein, daß (seinerzeit) eine "höhere" Macht die Aktionen gesetzt hat, die zur Produktion des zu analysierenden Materials führen und wir diesen Vorgang nun "rückgängig" machen, also reaktionär handeln, um die Information zu gewinnen die uns sagt was, wie zusammen gefügt wurde.

Wir müssen den "Inhalt" dieses Symbols, also Form und Materie in meßbare Größen umwandeln, um aus subjektiven Aussagen schließlich kategorische Objektivitäten zu machen.

Verallgemeinern wir den Clausius'schen Entropiegriff, den er auch den "Verwandlungs-Inhalt" nannte (wobei er aber die Verwandlung von Arbeit in Wärme meinte) und verbinden wir ihn mit den Hartley'schen und Shannon'schen mathematischen Theorien zur Kommunikation, so kommen wir zu den Anwendungsmöglichkeiten der Informationstheorie in der Chemie und zu neuen Aspekten der analytischen Chemie. Allerdings verlangt die moderne analytische Chemie auch sinnvolle Einbeziehung der System-, und Spieltheorie, um die aus dem Wechselspiel zwischen Probe und Reagenz und aus den Übergängen von Mikro-, zu Makrozuständen resultierenden Signale in relevante Informationen zu verwandeln. Dabei müssen wir uns stets vor Augen halten, daß die vorliegende Probe immer der makroskopische Zustand einer großen Auswahl definierter, aber oft noch nicht bekannter und daher eine Black-Box darstellende Anordnung von Mikrozuständen ist. Durch Messung mehr oder minder spezifischer Signale, die sich bis vor wenigen Jahren *in praxi* auch nur im makroskopischen Bereich bewegten, mußte mehr auf induktive als deduktive Art auf Materie und Form geschlossen werden.

Die Aussage:[12]

Probe ist Materie und Information

ist mehr als eine Proposition, sie ist im Sinne der analytischen Chemie eine Theorie und hat logischen Sinn. Es ist die Aufgabe der analytischen Chemie, die sowohl chemische als auch physikalische Reagenzien benutzt, den herrschenden Informationsmangel durch "Freisetzung" der Information zu beseitigen. Informationsmangel ist auch Unsicherheit, bzw. geringe Wahrscheinlichkeit der Deckungsgleichheit von *rei et intellectus*.

Die Freisetzung der Information aus materiellen Systemen erfolgt durch Zustandsänderungen von Systemelementen. Diese Zustandsänderung erfolgt nach thermodynamischen Gesichtspunkten und Gesetzen und führt dazu, daß das System von einem weniger wahrscheinlichen in einen wahrscheinlicheren Zustand transformiert wird. Die Verfolgung dieser Zustandsänderung ist der Meßvorgang, der meist erst nach Interpretation des Signals als "echte" Information erscheint. De Maeyer[13] schreibt z.B. "... Szilard zeigt, daß ein (derartiger) Meßprozeß, wenn er durch physikalische Vorrichtungen beliebiger Art realisiert wird, mit einer Entropieerzeugung verknüpft ist, die mindestens gleich oder größer ist als die Entropieverringerung die durch Verwertung des Meßergebnisses maximal erzielbar ist...".

In der Sprache der Analytischen Chemie heißt dies aber nicht mehr und nicht weniger, als daß das (transformierbare und transportierbare) Signal in Raum und Zeit über eine Koinzidenz mit einer, mehr oder minder willkürlichen Skala zur Information und zum Wissen führt. Weiters dürfen wir nicht außer Acht lassen, daß Information drei Aspekte aufweist, die wiederum alteregoistische betrachtet werden dürfen.

1. Mathematische–quantifizierbar–abstrakt (Hartley, Shannon, Wiener).

Tabelle 3.

Definition der Analytischen Chemie in bezug auf	
Philosophie (allgemein)	*Via ad congruendum rei et intellectus.*
Naturwissenschaft	Transformation der latenten Information einer Probe in aktive und verwertbare.
Systemtheorie[15]	Ein System aus mindestens 3 Elementen (Probe und Reagenz) und einer Relation zur Informationsgewinnung.
Pragmatik[15]	Die synoptische mikro- und makroskopische Betrachtung und Aufbereitung der material- und reagenzabhängigen Signale aus den Wechselwirkungen von Probe und Reagenz zur Aufklärung eines (materiellen) Problems.

2. Physikalisch–chemisch–konkret (Maxwell, Boltzmann).

3. Hermeneutisch–semeiotisch (von Weizsäcker, Monod, Eigen).

Der letzte genannte Aspekt besagt, daß Information nur etwas ist, was verstanden wird, bzw. wieder Information erzeugt (von Weizsäcker). Im zweiten, teilweise aber auch im ersten, sind die Beziehungen zwischen Informations-, Energie- und Wahrscheinlichkeitstheorie enthalten, die in jüngster Zeit (De Maeyer "Energiebedarf der molekularen Informations übertragung"[13]) stark in den Vordergrund getreten sind, und der erste, meist behandelte Aspekt, ist die Grundlage der alten und neuen Nachrichten-, bzw. Kommunikationstheorien. Alle drei sind aber auch, in alteregoistischer Synoptik, eine Grundlage der Analytischen Chemie. Das oftmalige Ineinanderfließen der drei Aspekte und die Tatsache, daß im 3. Aspekt der Wiener'sche Satz: "Information ist weder Materie noch Energie" als die Wandlung des (sehr wohl durch Materie und/oder Energie hervorgerufenen) Signals zur Information enthalten ist, ist im wesentlichen auch eine weitere Grundlage der Analytischen Chemie. Jedes reaktive System (und ein anderes ist in der Analytischen Chemie nicht brauchbar) ist eine Kommunikationskette, gehorcht der Thermodynamik und produziert aus jeweiligen Zustandsänderungen im materiellen Bereicht primär Signale, und daraus ergibt sich erst die überaus komplexe und komplizierte Situation der Informationsgewinnung. Die Signal- und die daraus folgende Informationsgewinnung ist ihrerseits aber die Grundlage der Automation und Kybernetik. Hier beginnt sich bereits abzuzeichenen, daß die moderne Analytische Chemie wohl die wichtigste Daten- und Informationslieferantin ist.

Erst wenn die Analyse des (synthetisierten) Produktes im Einklang mit der Theorie steht, kann das Problem als gelöst betrachtet werden. Um richtig und voll erkennen und beweisen zu können, müssen wir in allen möglichen Bereichen analysieren, d.h. aber konkret für die Naturwissenschaften: Wir müssen dem jeweils in Frage stehenden materiellen Gegenstand (der Probe) eine tiefe Bedeutung geben.

Für uns Analytiker heißt dies, daß die Probe das höchste Gut ist, weil sie die gesamte Information enthält. Wenn wir uns dies vor Augen halten, so gibt uns die Formulierung

$$\text{Probe} = \text{Materie} \rightleftharpoons \text{Energie} + \text{Information}$$

nicht nur sofort den Hinweis zu neuen Betrachtungsweisen, sondern auch die Rechtfertigung der bereits aufgestellten Forderung[14]:

materiam testendam ne mutaveris

Analysieren heißt also auch die in der Probe "gebundene" ("tote, "schweigende", "ruhende", "latente", "statistische") Information in "freie" ("lebendige", dynamische", "sprechende") überführen.

Denken und handeln in Systemen, die Anwendung der allgemeinen und der speziellen Wahrscheinlichkeitstheorie (letztere z.B. auch in Form der Spieltheorie) verbunden mit ausgiebigem Gebrauch von Metasprachen (und deren Beziehungen zu unseren natürlichen Sprachen) sind seit eh und je in der Analyse beinhaltet, doch nicht immer bewußt quantifizierend und beschreibend verfolgt worden. Jetzt aber, im Hinblick auf die "Überflutungsgefahren" und dem Mensch–Maschine Dialog, sind sie unbedingbare Notwendigkeit geworden.

Wenn wir wollen, daß auch in Zukunft die Maschinen nicht uns, sondern wir sie beherrschen, wenn wir nicht in einer Papierflut, genannt Information, ersticken wollen und wenn wir den technischen und sozialen Fortschritt durch Einbeziehung der Automation in die Analytische Chemie weiterhin fördern wollen, dann müssen wir—besonders wir Analytiker —neben den Metasprachen der Naturwissenschaften, Mathematik, Informatik, auch die Philosophie in unsere Betrachtungen in Lehre und Praxis aufnehmen. Dies auch dann, wenn worübergehend manche Betrachtungsweisen irrational anmuten.

Zusammenfassend sei die Frage: "Was ist Analytische Chemie", mit einigen Kurzdefinitionen beantwortet (Tabelle 3).

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Summary—To clarify the position of analytical chemistry in science, some philosophical views are quoted and brief definitions proposed.

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THE DETERMINATION OF TRACES OF O, N AND C IN THE REFRACTORY METALS Mo AND W—AN INTERNATIONAL EFFORT

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Summary—The influence of traces of O, N and C on the physical and especially the mechanical properties of the refractory metals Mo and W is discussed. The technological and economic importance of determination of O, N and C in Mo and W is elucidated. The Commission of the European Communities launched a relevant multidisciplinary Community Programme as early as 1969. The present state, within this programme, of the determination of O, N and C in Mo and W is outlined. Additional studies by the refractory metals group of the chemistry section of the Gesellschaft Deutscher Metallhütten and Bergleute (GDMB) are also reported on.

Oxygen. Two round-robin tests were conducted by the "non-metals in refractory metals" group of the Community Bureau of Reference (BCR) for the determination of oxygen in molybdenum. Reducing fusion, 14-MeV neutron-, photon- and charged-particle activation analysis yielded comparable results of about 15 ppm O. Homogeneity studies were conclusive and the reference material was certified and is available from BCR. Oxygen concentrations in tungsten turned out to be even lower, certainly below 5 ppm. Only activation analytical methods will be adequate to determine the true oxygen content and work in this direction is being undertaken.

Nitrogen. Relevant BCR round-robin tests for traces of N in Mo and W were not conclusive. Discrepancies were also found in a first round-robin test by the GDMB. It was possible, however, to reveal systematic errors frequently encountered in the classical Kjeldahl method, which turned out not to be applicable to the determination of nitrogen below 10 ppm. Only a newly devised micro-Kjeldahl method is capable of determining nitrogen down to 1 ppm and results for Mo are in good agreement with those of fusion methods. Nitrogen contents in W are presumably in the 100 ppM range and only determinable by ultrahigh-vacuum diffusion extraction and activation methods.

Carbon. Carbon contents in Mo and W are also often presumably in the range of 1–10 ppm and thus not determinable by classical combustion methods. Additionally, discrepancies occur between results of combustion in resistance-heated furnaces with temperatures up to 1300° and in high-frequency induction furnaces with temperatures up to 2000°. The GDMB-group is investigating this phenomenon.

The physical and especially the mechanical properties of the refractory metals molybdenum and tungsten are strongly influenced even by ppm amounts of oxygen, nitrogen and carbon.[1] For all three trace contaminants, the solubility in Mo and W at room temperature is extremely low. For O, the solubility in Mo and W ranges around 1 ppm, whereas for N, solubilities far below the 1 ppm level are probable. Carbon solubilities presumably range around 1 ppm, too. In practice, Mo and W are usually supersaturated with respect to O, N and C and hence brittle at room temperature. The transition temperature for the ductile–brittle change is most strongly affected by O, whereas N and C exert smaller effects. Because of the low solubility, O, N and C are mostly present in Mo and W as oxides, nitrides and carbides, partly bound to metallic trace contaminants also present. The oxides, carbides and nitrides in turn exert different effects if present within crystal grains or at grain boundaries. The picture becomes still more complex if the influence of the state and degree of dispersion of the oxides, nitrides and carbides is also considered. Exact data on the separate influence of O, N or C on Mo and W are not available because all three elements are usually present simultaneously and their combined effects may be different from their separate effects. Furthermore, Mo and W are usually produced by powder metallurgy methods and the mechanical properties of such materials are primarily defined by the history of their thermal and mechanical treatment. Topochemical microanalysis by Auger electron spectroscopy and/or secondary-ion mass-spectroscopy is still in its infancy.[2–4] Interpretations of results obtained so far vary from author to author. It is hoped, however, that these powerful methods of topochemical microanalysis will—in combination with classical methods of bulk trace analysis—shed some light on these very complex problems of the influence of traces of O, N and C (in various binding states and forms of distribution) on the properties of Mo and W.

It is also of great economic and technological importance to know the exact bulk contents of O, N and C present in Mo and W. This was discussed in detail by Kraft[5] for O and by Albert[6] for N. Some technological implications of the determination of C in Mo and W are worth mentioning. Carbon is an element of particular concern for the production of fine Mo and W wires and foils. Large amounts of it in the form of graphite or of a viscous organic

compound are used to prevent oxidation in the hot-drawing stages. This produces a significant carbon deposit on the surface of the wire, with the formation of carbides below the surface. In the subsequent production processes most of the carbon is removed by various heat treatment operations. It has been shown that large quantities of carbon adversely affect the performance of tungsten filaments in incandescent lamps.[7] It is also known from the production of fine molybdenum wires that higher amounts of carbon lead to frequent breaking in later cold-drawing stages. The same applies to thin Mo and W foils, where carbide inclusions lead to holes in the foil. The determination of carbon in thin wires and foils is complicated by the inhomogeneity of the carbon distribution and by the difficulty of proper etching of thin specimens.[8] For molybdenum electrodes which are used in the glass industry to heat the glass baths, a rigorous control of the carbon content is necessary to prevent gassing of the electrodes by the formation of CO. This can also happen with molybdenum ribbons and wires leading through the glass base of incandescent lamps, resulting in gas leakage in the lamp.

The materials specifications of Metallwerk Plansee guarantee maximum contents of 50 ppm O, 10 ppm N and 30 ppm C for pure compact molybdenum metal and 30 ppm O, 10 ppm N and 30 ppm C for pure compact tungsten metal. The amounts of O, N and C usually present are much lower than these guaranteed values. Quality control analyses carried out quarterly since 1974 show that for Mo, the average O values range from 10 to 20 ppm, the C values are about 10 ppm or lower and for N only the detection limit of *ca.* 1 ppm is usually found. For W, values of 5–10 ppm O are typical, C values are again mostly below 10 ppm and for N the detection limit is ordinarily found.

Economic aspects

Some economic aspects of the production and industrial significance of molybdenum and tungsten products are also worth mentioning. The production and consumption of Mo and W are very much dependent on overall economic conditions, especially those in the metal-working industry. Mo and W are subject to relatively wide price fluctuations. This is predominantly due to their high strategic significance (U.S. stock piles), low consumption in comparison with more common metals, effects of novel fields of application, speculation, and political decisions and changes. Thus, the price of W nearly doubled after the U.S. government stopped exporting W stock-pile reserves in 1970.

Only a small amount of the Mo and W ores mined is manufactured into pure metals or their alloys. The largest users of Mo in the western world are the U.S.A. and Europe, and Europe may already have surpassed the U.S. Total world consumption of Mo in 1976 amounted to *ca.* 90000–92000 tons of the metal. In the countries of the western world, 55% of the Mo is used for low-alloy steels, up to 21% for the production of stainless steels, up to 6% for iron and steel castings and only 18% for uses other than in the steel industry. Superalloys require 5%, and a further 10% are used in non-metallurgical applications, principally as lubricants (MoS_2, *ca.* 6%) and as catalysts for, *e.g.*, coal liquefaction or gasification. Only 3.5% are at present used for metallic Mo and its alloys. For the western world this corresponded to 3400 tons of Mo metal in 1974 and 3200 tons in 1976. Up to 1990, the Mo consumption for the production of the metal and its alloys is expected to rise slightly to 4% of the total Mo consumption for the western world, *i.e.*, to 5700 tons.[10] A shortage of Mo is not expected before 1990.

The most important application of tungsten is in the hard metal industry. Approximately 50–55% of the worldwide extraction is used for production of WC as the most important raw material for the overall hard metal production of *ca.* 17000 tons per year. Another 18–20% is used for tool steels, and small amounts for some types of stainless steel. Superalloys require another 6% while 5% go into chemical applications and 15% are used for the production of metallic W and its alloys (which amounted to *ca.* 5400 tons of the metal in 1976).[10] Tungsten extraction as a whole dropped from 34000 tons in 1961 to 27000 tons in 1963–1965 and only reached the 1961 level again in 1970. In 1976, production was about 36000 tons, resembling the 1971 total. It is expected that the total demand for W will rise to 58500 tons by 1990.[11] The semidynamic lifetime of certain and probable world resources for W was calculated to be *ca.* 30 years on the basis of a yearly rate of increase of 3.4% in worldwide demand.[11]

An extraordinary feature of Mo and W metal prices is their variation over several orders of magnitude depending upon the relevant degree of forming. Molybdenum prices at present range around DM 120/kg for sheet, DM 700/kg for foils and DM 1250/kg for fine wires (40 μm diameter).

For W, approximate costs are DM 300/kg for sheet and DM 1100/kg for foils, whereas for highly intricate helices for incandescent lamps, prices can reach DM 10000/kg. Table 1 illustrates the almost exponential rise of costs for the later production stages of fine wires and helices. This explains the stringent demand for proper chemical characterization of W and Mo metal, especially with respect to the analysis for O, N and C in order to minimize the very costly waste in manufacture of fine wires and foils.

The organization of relevant round-robin tests

The technological and economic implications of the determination of O, N and C in Mo and W (among a long list of other metals) were realized by the Commission of the European Communities a long time ago. As early as 1969, a relevant multidisciplinary programme was started.[13] It was also recognized in

Table 1. Relation of costs to stage of production of tungsten helices for incandescent lamps.[12]

Production of	% of total production costs
Tungsten oxide from ore	1.8
Metal powder from oxide	1.9
Metal rod from powder	1.6
Coarse wire from rod	5.3
Fine wire drawn from coarse wire	18.6
Double helix from fine wire	70.8

a general survey within the then six countries of the EEC that there is a stringent need for reference materials for determination of "gas" and carbon contents.[14] This paper summarizes the work done up to now on O and N determination in Mo and W by the working group on non-metals in refractory metals, set up by the Community Bureau of References (further referred to as "NM in RM"-group; scientific secretary: J. Pauwels, CBNM Geel, Belgium; chairman: J. Hoste, Rijksuniversiteit Gent, Belgium). It also reports on supplementary investigations carried out by the refractory metals group of the chemistry section of the Gesellschaft Deutscher Metallhütten- und Bergleute (GDMB) on N and C determination in Mo and W.

OXYGEN IN MOLYBDENUM

Two round-robin tests were conducted by the "NM in RM"-group for the determination of bulk oxygen in a molybdenum reference material. However, many important questions had to be solved beforehand in order to start a meaningful round-robin test and to evaluate its results properly.

The surface treatment of samples before analysis is an important factor in conventional assay techniques since the presence of surface contamination may affect the results of bulk analyses for O, N and C to an appreciable extent. The various possibilities of surface treatment were discussed, investigated and sorted out, and the reliable ones were optimized. Low-energy charged-particle activation-analysis was employed to determine correction factors for residual surface contents of O, N and C for the optimized surface treatment procedures and for a range of metals.[15] The residual surface-oxygen content of freshly etched Mo-samples (etching with hydrofluoric acid/nitric acid, subsequent washing with hydrochloric acid, water and methanol, and drying) was found to be 0.2–0.4 $\mu g/cm^2$.

Homogeneity studies were required to ensure the utility of the material to be certified. Sintered molybdenum in the form of 8 rods 26 mm in diameter and *ca.* 75 cm in length was supplied by Metallwerk Plansee and was found to be appropriate as reference material by 72 preliminary 14-MeV neutron-activation analyses on 8 samples distributed over the batch. It was concluded that the macrohomogeneity could be guaranteed to ± 1.8 ppm or better, this value being essentially limited by the precision of the method used. Charged-particle activation-analysis revealed that the microhomogeneity (on a 30-mg scale) is of the same order of magnitude.[16]

Finally, different aspects of organizing and executing intercomparison tests of chemical and/or physical quantities for reference materials had to be discussed, and a sequence of statistical tests was developed.[17]

The participants in the final round-robin test for the certification of bulk oxygen in the molybdenum reference material are listed in Table 2, and the results in Table 3.

The determination of oxygen in Mo with 14-MeV neutrons has been described in detail[18] and was carried out by three laboratories. Relevant experimental conditions and the correction factors applied are also described elsewhere.[16] A common mean value of 14.3 ppm O and a standard deviation of 2.4 ppm were calculated from the data given in Table 3 for the 14-MeV neutron-activation analysis.

The determination of oxygen by charged-particle activation-analysis was described by Engelmann.[19] ^3He and α-activation analysis was applied to the analysis of Mo for oxygen by 2 laboratories (for experimental details see ref. 16), with the results listed in Table 3.

The determination by photon-activation analysis was also described by Engelmann[19] and was used by two laboratories; the results listed in Table 3 give a common mean value of 14.0 ppm O and a standard deviation of 1.3 ppm.

The results from the four laboratories using inert-gas fusion show a homogeneous and normal distribution [$D = 0.084 < D(0.05) = 0.128$], fairly comparable variances [$\chi^2(0.05) = 7.8 < \chi^2 = 8.7 < \chi^2(0.01) = 11.3$], and equivalent mean values ($\delta = 0$). A common mean value of 15.0 ppm O and a standard deviation of 1.7 ppm were calculated.

One laboratory, which produced obviously too low results, was regarded as using unsatisfactory extraction conditions and was not used again. Its results were not included in Table 3.

The 10 laboratories using vacuum fusion show normally distributed results [$D = 0.066 < D(0.05) = 0.081$], but the variances ($\chi^2 = 29 > \chi^2(0.01) = 22$) and means ($\delta = 1.5$ ppm) are less comparable. Nevertheless, $\delta = 2$ ppm being still acceptable, a common mean value of 14.7 ppm O and a standard deviation of 2.1 ppm can be calculated. It has to be pointed

Table 2. Participants in the final round-robin test for the certification of the oxygen bulk content of a molybdenum reference material

I. SAMPLE PREPARATION

J.R.C., Central Bureau for Nuclear Measurements, Geel, Belgium (J. van Audenhove)
Metallwerk Plansee AG., Reutte, Austria (E. Lassner, H. M. Ortner)

II. SURFACE ANALYSES

Groupe de Physique des Solides de l'Ecole Normale Supérieure, Paris, France (D. David)
Université de Liège, Institut de Physique Nucléaire, Liège, Belgium, (L. Quaglia, G. Weber)

III. HOMOGENEITY TESTS

Rijksuniversiteit Gent, Institut voor Nucleaire Wetenschappen, Gent, Belgium (J. Hoste, C. Vandecasteele)

IV. CERTIFICATION ANALYSES OF BULK OXYGEN

1. 14-MeV neutron-activation analysis

Rijksuniversiteit Gent, Institut voor Nucleaire Wetenschappen Gent, Belgium (J. Hoste, C. Vandecasteele)
Bundesanstalt für Materialprüfung, Berlin, GFR (B. F. Schmitt)
Centre de Recherches Pechiney, Voreppe, France (G. Beurton)

2. Helium-3 activation analysis

C.N.R.S., Service du Cyclotron, Orléans, France (P. Albert, J. L. Debrun)

3. α-Activation analysis

Université Claude Bernard, Institut de Physique Nucléaire, Villeurbanne, France (J. Tousset)

4. Photon-activation analysis

Centre d'Etudes Nucleaires de Saclay, Gif-sur-Yvette, France (C. Engelmann)
Bundesanstalt für Materialprüfung, Berlin, GFR (B. F. Schmitt)

5. Inert-gas fusion extraction

Metallgesellschaft AG., Frankfurt, GFR (G. Kraft)
Centre d'Etudes Nucleaires de Fontenay-aux-Roses, France (G. Baudin, Mme. Desreumaux, R. Marcovici)
Bundesanstalt für Materialprüfung, Berlin, GFR (H. Pohl)
Centre d'Etudes Nucleaires de Grenoble, France (Corgier)

6. Vacuum-fusion extraction

Métallurgie Hoboken-Overpelt, Hoboken, Belgium (M. Bomans)
Max Planck Institut für Metallforschung, Laboratorium für Reinststoffe, Schwäbisch Gmünd, GFR (E. Grallath)
Ugine Aciers, Ugine, France (R. Loude)
Centre d'Etudes Nucléaires de Bryères-le-Châtel, Montrouge, France (Malherbe)
Centre d'Etudes de Valduc, Is-sur-Tille, France (Fest)
Joint Research Centre Ispra, Chemistry Division, Ispra, Italy (A. Colombo)
National Physics Laboratory, Teddington, United Kingdom, Division of Chemical Standards (E. J. McLaughlan)
Ugine Carbone, Grenoble, France (Czarnul, Chapelard)
Metallwerk Plansee AG., Reutte, Austria (H. M. Ortner)
Imperial Metals Industries Ltd, Birmingham, United Kingdom (D. M. Peake)

V. STATISTICAL EVALUATION

Joint Research Centre Ispra, CETIS, Ispra, Italy (L. Haemers, J. Larisse)

out that for carrier-gas as well as vacuum-fusion extraction, quite a variety of measurement parameters was applied, practically the whole range of commercially available instruments being used.[16] Extraction temperatures ranged from 1950° to 2600° and Pt, Ni, Ni–Sn, Ce–Ni were used as bath metals in various bath-to-Mo ratios. In view of this, the agreement of results can be considered very satisfactory.[20]

For the 21 laboratories ($n = 300$) using 6 completely different methods of analysis, no outlying variances (Cochran[17]) or outlying means (Dixon[17]) were found and the total population is approximately normal [$D(0.05) = 0.051 < D = 0.053 < D(0.01) = 0.059$].

A one-way analysis of variance leads to $F = 4.47 > F(0.01) = 2.19$, repeatability $\sigma_r = 1.9$ ppm O and reproducibility $\sigma_R = 2.1$ ppm O. This is fully acceptable from a technical point of view.

Hence, the unalloyed Mo reference standard material analysed could be certified as having a bulk oxygen concentration of 14.7 ppm, with an uncertainty of 2.1 ppm. The reference material (BCR—No. 23 "Oxygen in Molybdenum") is available in disc form (diameter 26 mm, thickness 9 mm) or as 1-g cubes in bottles containing 25 cubes.

OXYGEN IN TUNGSTEN

It is well known from production control as well as from the quarterly quality-control analyses at Metallwerk Plansee that the oxygen content of W is usually considerably lower than that of Mo. This was also confirmed in a first round-robin test by the "NM in RM"-group in 1972–73. The oxygen concentration in the W metal used was between 1 and 5 ppm.

Table 3. Results of the final round-robin test for the certification of the oxygen bulk content of the molybdenum reference material

Lab. No.	Method applied	results, *ppm* O $\bar{x}$	s	n
1	14-MeV neutron AA	14.6	2.8	36
2		14.5	2.4	24
3		13.4	1.4	24
4	^{3}He-AA	16.1	0.7	12
5	α-AA	16.7	2.2	12
6	Photon-AA	13.0	0.5	12
7		15.1	0.8	12
8	Inert-gas fusion extraction	15.3	0.9	12
9		15.2	1.5	12
10		14.9	2.2	12
11		14.6	2.0	12
12	Vacuum-fusion extraction	15.4	1.4	12
13		13.5	1.2	12
14		15.7	2.6	12
15		14.7	1.3	12
16		14.7	2.0	12
17		16.6	2.8	12
18		14.9	0.6	12
19		13.0	1.7	12
20		15.3	2.2	12
21		12.6	1.8	12

Further work performed in 1973–74 set the probable value at 2 ± 1 ppm. This is already beyond the reach of most fusion-extraction methods with detection limits between 1 and 5 μg of O, which correspond to 1–5 ppm O for the usual sample weights of *ca.* 1 g.[20]

A new and larger batch of W metal produced by powder metallurgy was supplied by Metallwerk Plansee in the form of 4 bars 26 mm in diameter and *ca.* 70 cm in length, in 1975. Surface and homogeneity studies of this batch were performed by the laboratories indicated in Table 4. After an etch with hydrofluoric acid/nitric acid (1:4) for 5 min and washing with water and methanol, the surface oxygen content found[15] was 0.1–0.3 μg/cm^2. Homogeneity studies confirmed that at least 3 of the 4 bars were sufficiently homogeneous with respect to bulk oxygen (*cf.* Table 5). Hence, samples for the round-robin test were taken only from those bars which showed a fairly homogeneous oxygen distribution (*i.e.*, samples A1–A4). Nevertheless, the results shown in Table 5 are not at all conclusive. Neither the activation-analysis results nor the fusion-extraction results as a group exhibit satisfying agreement. Most laboratories applying fusion-extraction methods simply found values that were the detection limits. The values from laboratory No. 7 also lie very close to the relevant detection limit of 4.5 μg of oxygen, although they exhibit a remarkably good standard deviation of 1.4 ppm (the usual value is at least 1.6 ppm), which encouraged this laboratory to report the values actually obtained rather than merely the detection limit.

The overall results prove that considerable efforts are still necessary to further develop methods for a safe determination of the bulk oxygen contents of the order of 1 ppm or even lower which are presumably present in compact unalloyed W metal. Fusion-extraction methods will be excluded from further investigations because their sensitivity, of at best 1 μg of O, is insufficient for a precise determination of oxygen at the 1-ppm level. Further work with 14-MeV neutron-activation analysis and charged-particle activation-analysis is in progress.

From a technical point of view it is rather astonishing that the production of W by powder metallurgy yields material with such low oxygen contents. The situation is similar to that for aluminium, which is also at the stage of being certified as reference material for bulk oxygen content and for which successively lower oxygen values were found, finally ending up with bulk oxygen contents at the 50 ppM level (1 ppM = 1 part per milliard).[13]

NITROGEN IN Mo AND W

Several round-robin tests of the determination of nitrogen in Zr, Ta, Mo and W were organized by the BCR from 1972 onwards. Except for Zr, the results of these tests were not conclusive. Generally, low results were obtained for Mo and W by fusion-extraction methods, photon-activation analysis and spark-source mass-spectrometry. Results 5–10 times as high were found with the Kjeldahl method and alkaline fusion.[13] Further BCR work then concentrated on the certification of N in Zr and the problem of nitrogen determination in Mo and W was taken up by the refractory metals group of the chemistry section of the GDMB in 1975. The results of this work were discussed in detail by Grallath and Ortner.[21] The following methods were applied: classi-

Table 4. Participants in the last round-robin test for the analysis of the oxygen bulk content of tungsten metal

I. SAMPLE PREPARATION

J.R.C., Central Bureau for Nuclear Measurements, Geel, Belgium (J. van Audenhove, J. Triffaux)
Metallwerk Plansee AG., Reutte, Austria (E. Lassner, H. M. Ortner)

II. SURFACE ANALYSES

Groupe de Physique des Solides de l'Ecole Normale Superieure, Paris, France (D. David)
Université de Liège, Institut de Physique Nucléaire, Liége, Belgium (G. Weber)

III. HOMOGENEITY TESTS

Laboratorium für Isotopentechnik, Gesellschaft für Kernforschung m.b.H., Karlsruhe (H. Vogg)

IV. DETERMINATION OF BULK OXYGEN

1. 14-MeV neutron-activation analysis

Rijksuniversiteit Gent, Institut voor Nucleaire Wetenschappen Gent, Belgium (J. Hoste, R. Kieffer, C. Vandecasteele)
Centre de Recherches Pechiney, Voreppe, France (G. Beurton)
Laboratorium für Isotopentechnik, Gesellschaft für Kernforschung m.b.H., Karlsruhe GFR (H. Vogg)
Institute für Radiochemie der Technischen Universität München, Garching, GFR, (R. Henkelmann, O. Kowarik, H. Bittner)

2. 45-MeV ^{4}He-activation analysis

Rijksuniversiteit Gent, Institut voor Nucleaire Wetenschappen, Gent, Belgium (C. Vandecasteele, R. Kieffer, J. Hoste)

3. Inert-gas fusion extraction

Bundesanstalt für Materialprüfung, Berlin, GFR (H. Pohl, K. Wandelburg)

4. Vacuum-fusion extraction

Max Planck Institut für Metallforschung, Laboratorium für Reinststoffe, Schwäbisch Gmünd, GFR (E. Grallath)
Metallwerk Plansee AG., Reutte, Austria (H. M. Ortner)
Joint Research Centre Ispra, Chemistry Division, Ispra, Italy (A. Colombo, R. Vivian)

V. STATISTICAL EVALUATION

Joint Research Centre Ispra, CETIS, Ispra, Italy (L. Haemers, J. Larisse)

Table 5. Results of the last round-robin test for the determination of the oxygen bulk content of tungsten metal

Lab. No.	Method applied	Sample No.	Results, *ppm* O $\bar{x}$	s	n
1	Homogeneity tests by 14-MeV neutron AA	A1	0.95	—	—
		A2	0.75	—	—
		A3	1.05	—	—
		A4	1.20	—	—
		A5	2.20	—	—
1	14-MeV neutron AA	A2	1.1	0.6	6
		A3	0.9	0.3	6
2		A1	0.82	0.26	6
		A3	inhomogeneous due to crystal faults		
3		A2	1.1	0.6	6
		A3	0.9	0.3	6
4		A1	3.0	1.9	6
		A2	1.4	1.6	6
2	45-MeV ^{4}He AA	A3	0.55	0.15	3
5	Inert-gas fusion extraction	A1	$\leqslant 1.5$	—	6
		A4	$\leqslant 1.5$	—	6
6	Vacuum fusion extraction	A1	$\leqslant 1$	—	12
7		A2	5.1	1.36	15
		A4	5.0	1.45	16
8		A1	$\leqslant 2$	—	6
		A3	$\leqslant 2$	—	6

cal and modified Kjeldahl methods (in particular, a newly developed micro-Kjeldahl method[22]), inert-gas and vacuum-fusion extraction methods and a newly designed ultrahigh-vacuum diffusion extraction method.[23] Nitrogen values obtained in the first round-robin test exhibited a scatter which was quite similar to that in previous BCR circular analyses, with values obtained by classical Kjeldahl methods being much higher than the fusion- and diffusion-extraction values and those obtained by the micro-Kjeldahl method. Therefore, possible shortcomings of the various Kjeldahl methods as well as the quantitative nitrogen recovery by the fusion- and diffusion-extraction methods were carefully examined. A second interlaboratory test showed that the nitrogen content of the Mo sheet investigated was 2 ppm, the content of the W sheet 0.5 ppm. As with oxygen, the nitrogen contents are generally still lower in W than in Mo. As a rule, classical Kjeldahl methods are not applicable to the determination of nitrogen contents below 10 ppm. Indeed, the detection limits of Kjeldahl methods frequently range considerably above 10 ppm, mainly because of contamination from the reagents and/or the laboratory atmosphere.[21] The micro-Kjeldahl method and the fusion-extraction methods are capable of determining nitrogen contents down to 1 ppm at best. The detection limits range from 1 to 3 μg of N.[21] The only available method within the refractory metals working group of the GDMB, for nitrogen determination in metals at sub-ppm levels, was the ultrahigh-vacuum diffusion extraction. Only by this method was it feasible to determine the nitrogen content of the W sheet. The good agreement between the nitrogen values obtained for Mo by the micro-Kjeldahl method and by the various hot extraction methods is the most reliable proof of the recovery of nitrogen by the extraction methods applied is quantitative.

These results make it seem a rewarding and fascinating task for the BCR to resume the project of nitrogen certification in Mo and W, with restriction of further round-robins to the most powerful activation-analysis methods, ultrahigh-vacuum diffusion extraction and possibly spark-source mass-spectrometry.

CARBON IN Mo AND W

Up till now, no round-robin tests of the determination of traces of carbon in Mo and W have been undertaken by the BCR, although it is intended to extend the activities of the "NM in RM" group to C in refractory metals. The certification of C in Zr is in progress. The problem of the determination of traces of C in Mo and W is being studied by the refractory metals group of the GDMB.

It might be thought that the determination of C in metals by classical combustion analysis in an oxygen stream is such a well-explored procedure that it should pose no problems, but this is not the case for traces of C in refractory metals.

The GDMB working group undertook a first interlaboratory test on the analysis of compact Mo for trace C in 1969–1971. Even after careful calibration with potassium hydrogen phthalate by all eight participating laboratories, the values obtained ranged from 1 to 10 ppm. It was concluded that the analysis for less than 10 ppm C in metals was not feasible by classical combustion methods. In the course of this work, Lassner thoroughly investigated possible sources of error of trace carbon determination in metals.[24,25] They can be classified into 3 categories.

(1) Errors due to improper sample preparation.

(2) Errors due to incomplete combustion or extraction losses of CO_2.

(3) Errors due to false measurement of CO_2.

In 1976, the problem was again taken up by the GDMB-group and a round-robin test was organized.

Errors due to improper sample preparation were eliminated by using a standardized etching procedure which was applied by all participants and which is the same as for the O and N determination in Mo and W. Residual surface carbon was found to range between 0.09 and 0.12 $\mu g/cm^2$ after the standardized etching procedure.[26]

Completeness of combustion is usually checked by instrument calibration with, *e.g.*, potassium hydrogen phthalate, sodium carbonate, sodium oxalate, or reliable certified reference materials such as low-carbon steels. There is, however, a basic difficulty if quantitative combustion of refractory metals is to be checked with these materials, because there are very pronounced differences in their combustion behaviour. In the case of Zr, a too-rapid combustion programme leads to the necessity to prefuse the Zr with C-free iron in order to prevent too fast oxidation. Mo oxidizes considerably more slowly than Zr and such precautions are unnecessary. Nevertheless, the addition of CuO in wire form is obligatory in order to reduce undue sublimation of the MoO_3 generated. Without the addition of CuO, tungsten oxidizes too slowly at temperatures below 1300°. Above 1300°, the oxidation of W becomes very rapid.

Until recently, it was believed that quantitative combustion is achieved by oxidizing 1-g samples of Mo and W in the presence of 2 g of CuO in resistance-heated furnaces at 1250–1300°. This situation changed with the advent of inductively heated furnaces. It was observed in the author's laboratory that striking discrepancies in carbon values occurred when results obtained by use of resistance-heated furnaces were compared with those obtained in inductively heated furnaces for the same sample materials. Some typical results are listed in Table 6. One possible explanation of these discrepancies could be that the lower values found with the resistance-heated furnaces are due to incomplete combustion at the considerably lower combustion temperature attained (*ca.* 1300°). The temperatures reached in HF-induction furnaces by the application of tungsten-grit as accelerator material presumably range around 2000°. Another explana-

Table 6. Some comparative results for traces of C in Mo and W and their oxides, obtained with the Woesthoff Carmhomat 12 G (resistance-heated furnace, 1300°) and with the Heraeus CSA-301-LC (HF-induction furnace, *ca.* 2000°): tabulated results are the arithmetic means of triplicate determinations

Material	C, *ppm* Heraeus CSA-301-LC	C, *ppm* Woesthoff Carmhomat 12 G	Difference, $\left(\frac{\text{Heraeus–Woesthoff}}{\text{Heraeus}}\right) \times 100\%$
compact sintered Mo	25	<5	>80
compact sintered W	23	17	26
Mo-powder	83	41	49
W-powder	28	6	79
W-grit	16	10	38
MoO_3	122	not determinable owing to vigorous sublimation	
WO_3	24	6	75
tungsten blue oxide	115	90	22

tion could be that the blank values are raised in HF-induction furnaces by the excessive corrosion of the cup material in the presence of larger amounts of Mo and W, which causes very high and frequently varying combustion temperatures. Corrosion is additionally favoured by the high acidity of MoO_3 and WO_3 melts.

Our observations on these discrepancies can be summarized as follows.

(*a*) If differences occur, the values obtained with the Woesthoff apparatus are always lower than those obtained by HF-induction heating in the Heraeus apparatus.

(*b*) No constant differences have been observed for any sort of Mo or W material investigated. As can be seen from Table 6, differences may vary within 20–80% or more. Sometimes, however, no differences are observed at all.

(*c*) No such differences are observed for the certified reference steels which have to be used for calibration of the Heraeus CSA-301-LC, as can be seen from Table 7.

Table 7, however, reveals another difficulty: for some of the certified reference materials, especially in the region of carbon contents between 10 and 100 ppm, the values obtained do not agree with the certified values. The values obtained in our laboratory with the Woesthoff apparatus were determined after calibration with potassium hydrogen phthalate as primary standard. Two batches of the BAM-reference steel 131 were also found by Grallath to have a carbon content of 62 and 60 ppm (BAM 131—1/364 and BAM 131—1/585) when the instrument was calibrated with potassium hydrogen phthalate, $Na_2C_2O_4$ and CO_2.[27] This clearly demonstrates the stringent need for reliable certified reference materials for carbon, especially in the range of 10–100 ppm.

Table 8 compares the precision and obtainable detection limits with the resistance-heated Woesthoff Carmhomat 12G and the HF-heated Heraeus CSA-301-LC. In both cases, the absolute value of the blank is primarily determined by the amount and quality of the CuO and tungsten-grit used. As also observed by other laboratories, the precision obtained with resistance-heated furnaces is superior to that obtained with HF-induction furnaces. This is mainly because the energy uptake in the latter is variable, being a function of the types and weight ratios of metals present, their grain size distribution, shape and probably other factors not yet fully understood, as well as corrosion of the cup material as mentioned above.

Table 9 lists the participants in the latest GDMB round-robin test for the determination of bulk carbon in Mo and W. Table 10 gives the results.

The following conclusions can be drawn.

(1) The trace determination of bulk carbon—especially in refractory metals—remains problematic in the range below 20 ppm. This is not so for other materials, *e.g.* steels. A parallel round-robin for two

Table 7. Some comparative results for traces of C in certified reference steels, with the Woesthoff Carmhomat 12 G and the Heraeus CSA-301-LC: all values for $\bar{x}$ and s are in ppm (w/w)

Certified reference material	Certified values $\bar{x}$	s	v, %	Woesthoff Carmhomat 12 G $\bar{x}$	s	v, %	Heraeus CSA-301-LC $\bar{x}$	s	v, %
BAM-17/245	430	40	9.3	415	5.5	1.3	415	11	2.7_5
BAM-3a/441	393	12	3.0_5	380	4.8	1.3	385	13	3.3
BAM-8a/317	344	12	3.5	337	7.0	2.0	343	15	4.4
BAM-131-1/498	73	9	12	66	2.8	4.2	60	3.9	6.5
BAM-044-1/55	25	2	8.0	24.1	2.8	7.5	25.0	1.8	7.3
BCS-149/3	20	—	—	22	2.2	10	24	3.5	15
BCS-260/4	15	—	—	22	2.1	9	22	4.1	19
BAM-043-1/61	14	3	21	14.6	1.3	9	19	3.6	19

v = coefficient of variation.

Table 8. Comparison of precision and detection limits for the combustion determination of traces of C with the Woesthoff Carmhomat 12 G and the Heraeus CSA-301-LC

Concentration range, *ppm*	Woesthoff Carmhomat 12 G					Heraeus CSA-301-LC				
	s_r *ppm*	v_r %	$\bar{x}_{blank}$ (blank = porcelain boat + 2 g of CuO) μg C	s_{blank} μg C	detection limit† μg C	s_r *ppm*	v_r %	$\bar{x}_{blank}$ (blank = crucible + 1.5 g of W-grit) μg C	s_{blank} μg C	detection limit† μg C
10–100	2–4	20–4	5–10	2	6	3–7	30–7	5–10	3*	9
100–1000	4–20	4–2				7–20	7–2			

* This corresponds to the apparatus specification for precision of 3 μg.
† Detection limit defined by Kaiser as $3s_{bl}$.

Table 9. Participants in the latest round-robin test of the working group "refractory metals" of the chemistry section of the GDMB on the determination of bulk carbon in sintered compact Mo and W

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E. Grallath, Max Planck Institut für Metallforschung, Laboratorium für Reinststoffe, Schwäbisch Gmünd
O. Hilmer, H. C. Starck, Goslar
D. Hirschfeld, F. Krupp G.m.b.H., Krupp Forschungsinstitut, Essen
H. M. Ortner, Metallwerk Plansee A.G., Reutte, Tirol
M. Röhrl, Süddeutsche Kalkstickstoffwerke A.G., Trostberg
V. Scherer, Osram GmbH., München
H. Schneider, Kernforschungszentrum Karlsruhe, Institut für Material- und Festkörperforschung

certified reference steel standards from BAM (Berlin), *i.e.*, for AKP 043-1 and AKP 044-1 with carbon concentrations of 14 and 25 ppm respectively, yielded quite satisfactory results. Hence, the difficulties are specific for Mo and W.

(2) Laboratory 2 in Tabl 10 used sample weights of about 0.2 g whereas all other participants used sample weights between 0.5 and 2 g, mostly 1 g. The strikingly high standard deviation obtained by laboratory 2 by far exceeds the standard deviation of the method itself. This indicates a pronounced microheterogeneity. The relative variances obtained by the other laboratories range from 10–20% for 10–20 ppm carbon and mostly around 30% for carbon values below 10 ppm, which can be considered normal. Although homogeneity tests were performed before the round-robin test there still remains the principal question of partition of carbon in sintered Mo and W to be solved, because homogeneity tests when the content is in the region of the detection limit (as, especially, for C in W) can only reveal very significant heterogeneities. All that can be said is that the homogeneity at the 1-g level is significantly better than at the 200-mg level for the materials investigated.

(3) The discrepancies between values obtained with resistance-heated furnaces and HF-induction furnaces, which were discussed above, do not occur for the Mo and W sheet of this round-robin test.

All this calls for the application of activation-analysis methods, which do not face all the difficulties caused by combustion characteristics, are capable of a reliable carbon determination at or below the 1-ppm level, and can clearly solve the question of macro- and microhomogeneity at various levels.

CONCLUSION

Several years ago, a very prominent analytical chemist stated that the most stringent need of modern analytical chemistry—especially in trace analysis—is for accurate measurements of real-type samples with several methods.[28] It was also stated then that the predominant aspect of trace analysis is accuracy rather than precision. However, the only way to arrive at accurate results is by the conformity of such results obtained by different, independent methods. It is in this context that the work reported here represents an effort which to the author's knowledge is unique. Never before has the problem of trace analysis for O, N and C in refractory metals been studied by such a large group of experts experienced in very diverse fields of analytical chemistry. The combined application of a wide variety of activation-analysis methods together with classical methods has already led to surprising new insights into the trace contamination levels of Mo and W with respect to oxygen. Everybody in the field was more or less surprised by the extremely low oxygen content found in tungsten. It is greatly to the credit of the European Community that it initiated this work and sponsored it throughout the years.

On the other hand, the smaller and easily manoeuvrable "refractory metals" group of the GDMB succeeded in clearly demonstrating the limits of classical trace analysis for N and C in refractory metals and in showing that the true N and C contents, especially in W, are below these limits. Thereby, this group prepared the field for final round-robin tests to be conducted by the BCR, with application of only activation-analysis methods capable of trace analysis in the sub-ppm region.

It is this combined European effort which has ultimately led to the production of a most remarkable certified reference material for oxygen in Mo with a certified oxygen value of 14.7 μg/g and an uncertainty of only 2.1 μg/g. The certification of O in a refractory metal at such a level and with such a high degree of accuracy and precision is unsurpassed even by high-purity metals from NBS.[29] Should further work on the certification of O in W and on N and C in Mo and W be successful, these efforts will lead to still more outstanding reference materials with contents certified at presumably the sub-ppm level. Such low levels would make the certified materials important for evaluating instrument and system blanks. They would also be expected to be very valuable in the development of new or improved methods and techniques for extending the sensitivity of detection for the determination of O, N and C traces in various metals.

Everyone participating in this work knows how tedious these investigations were and always will be, and how complex the questions are which still await tackling. However, participation in this process of extending the methods and possibilities of analytical chemistry to their very limits in order to enlarge our

Table 10. Measurement parameters and results of the last round-robin test of the GDMB on traces of C in sintered compact Mo and W

Lab. No.	Apparatus	Combustion temperature, °C	Sample weight, g	Flux type	Flux quantity, g	Calibration with	Blank value total, µg	Blank value µg/g flux	Final round-robin test for sintered Mo n	Mo $\bar{x}$, ppm	Mo s, ppm	Mo v, % relative	Final round-robin test for sintered W n	W $\bar{x}$, ppm	W s, ppm	W v, % relative
1	Schoeps Coulomat CTA 5 C	1300	1	CuO	2	KH-phthalate	8	4	5	5	1.0	20	5	3.4	1.1	32
2	Woesthoff Carmhomat 12 G, adjusted for small sample weights	1300 and 1520	0.2	CuO	0.4	KH-phthalate	1	2.5	5	12	7.1	61	4	3.6	3.3	92
3	Schoeps Coulomat CTA 5 C	1250–1300	0.5	CuO	2	Na_2CO_3	3	1.5	5	13	1.4	11	4	3.0	1.0	33
4	Woesthoff Carmhomat 12 G	1300	1–2	CuO	2	KH-phthalate	8	4	6	18	3.3	19	6	8.3	2.3	28
5	(*a*) Woesthoff Carmhomat 12 G	1250	1	CuO	2	KH-phthalate	8–10	4–5	6	17	3.4	20	8	⩽5	—	—
	(*b*) Heraeus CSA-301-LC	*ca.* 2000	0.5–1	W-grit	1.5	Certified reference materials (steels)	5–10	3.3–6	10	15	3.1	21	8	(9.0) ⩽10	2.4	27
6	Schoeps Coulomat CTA 5 C	1300	1	CuO	2	Na-oxalate	9	4.5	4	11.5	2.1	20	6	4.8	4.3	90
7	Woesthoff Carmhomat 12 G	1300	1	CuO	2	Certified reference materials (steels)	8	4	4	11	1	9	4	6.7	1.9	28
8	Schoeps Coulomat CTA 5 C	1300	1	CuO	2	Certified reference materials (steels)	5.5–7.5	3	6	⩽10	—	—	5	⩽10	—	—

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knowledge of materials with a promising future, such as Mo and W, is in the author's belief one of the most exciting challenges of modern analytical chemistry.

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APPARATUR ZUR SÄULENELEKTROPHORESE IN NICHTWÄSSRIGEN LÖSUNGSMITTELN

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Zusammenfassung—Es wird eine Apparatur zur Säulenelektrophorese in nichtwässrigen Lösungsmitteln beschrieben, die ein Arbeiten bei Feldstärken bis zu 150 V/cm and Temperaturen bis −50° erlaubt. Zur kontinuierlichen photometrischen Auswertung der Trennungen dient eine Durchflußküvette mit zwei doppelten "Suprasil"-fenstern. Sie gestattet die Kühlung der Probe bis zum Detektorsystem. Getrennt werden Kaliumpolysulfide als Beispiel für hydrolyseempfindliche Salze, Thiocyanato(phenylendiamin)chrom(III)-Komplexe als Beispiel für wasserschwerlösliche Salze und aromatische Sulfonate als Beispiel für mit Kronenverbindungen komplexierte Salze.

Der Übergang von einer offenen Kammer[1,2] zur geschlossenen Säule bringt für die Elektrophorese in nichtwässrigen Lösungsmitteln erhebliche Vorteile. Diese sind: Verwendung auch niedrig siedender Lösungsmittel, Ausschluß von Luft und Feuchtigkeit, kontinuierliche Probenentnahme und Durchsatz größerer Mengen.

Im folgenden wird eine Apparatur beschrieben, die nur noch aus Glas besteht und somit die Verwendung aller gängigen organischen Lösungsmittel sowie die Beobachtung der Vorgänge in der Trennsäule, an den Elektroden und Membranen gestattet. Weitere Vorteile sind der einfache apparative Aufbau, das kleine Totvolumen und eine gute Kühlleistung, die Feldstärken bis zu 150 V/cm und Temperaturen bis zu −50° erlaubt. Außerdem ist die Kühlung der Probe bis zum Detektor möglich. Je nach Packung der Säule und Trenntemperatur dauert die Elektrophorese 30 min bis 5 h. Wegen ihres relativ guten Lösungs- und Ionisierungsvermögens dienen als Lösungsmittel hauptsächlich Ameisensäure, Eisessig, Methanol, Ethanol, Propanol-2, Acetonitril, *N*,*N*-Dimethylformamid und Nitrobenzol. Geeignete Leitsalze sind LiCl, NaSCN und KSCN, da sie in den meisten der angegebenen Lösungsmittel Löslichkeiten $>0{,}1M$ besitzen.

EXPERIMENTELLER TEIL

Verwendete handelsübliche Geräte

Hochspannungserzeugung. Power Supply Type 3371 A, LKB (Bromma, Schweden).

Kühlung. Ultra-Kryomat K-40 DW, Meßgerätewerk Lauda (Lauda).

Photometrische Auswertung. Spektralphotometer PM 2 D, Zeiss (Oberkochen) mit angeschlossenem Kompensationsschreiber Polycomb 2, Hartmann und Braun (Frankfurt).

* Für finanzielle Unterstützung danken wir der Deutschen Forschungsgemeinschaft, Bonn-Bad Godesberg.

Aufbau der Apparatur

Die Apparatur besteht aus dem unteren Elektrodengefäß, einem Zwischenstück, der Probenentnahmevorrichtung, der eigentlichen Trennsäule, dem oberen Elektrodengefäß und einem Vorratsgefäß (Abb. 1).

Unteres Elektrodengefäß. Es besitzt ein Volumen von 200 cm^3 und dient gleichzeitig als Standgefäß. Die seitliche Schliffhülse faßt einen Teflonkern, in den ein Platindraht als Elektrode eingepaßt ist. Sie ist über einen angelöteten BNC-Stecker mit der Stromquelle verbunden. Durch das angeschmolzene Steigrohr von 1,0 cm Durchmesser entweichen die Elektrolysegase. Auf der zweiten Schliffhülse sitzt das Zwischenstück.

Zwischenstück. Es dient zur Kühlung der Probenentnahmevorrichtung, hat eine Länge von 9 cm, einen Innendurchmesser von 0,33 cm und ist mit einem Kühlmantel (Außendurchmesser 1 cm) umgeben, dessen unterer Kern als Hohlschliff ausgelegt ist. Zum Abdichten werden genormte Teflonschuhe (NS 14.5) benutzt. Der obere Teil des Zwischenstücks ist als Planschliff gearbeitet. Auf ihm liegt die untere Membran der Probenentnahmevorrichtung.

Probenentnahmevorrichtung. Sie besteht aus einem runden, 1 cm hohen, biplan geschliffenen Glasblock, der vertikal und horizontal durchbohrt ist (Abb. 2).

Der Innendurchmesser der vertikalen Bohrung beträgt 0,33 cm und entspricht dem des Zwischenstücks und der Trennsäule. An die horizontale Bohrung (Innendurchmesser 0,33 cm) sind die gegenüberliegenden Zu- und Ablaufstutzen mit 0,25 cm Innendurchmesser angeschmolzen. In den biplanen Oberflächen des Glasblocks befinden sich eingeschliffene Vertiefungen, in die die beiden scheibenförmigen Membranen genau hineinpassen. Die obere Membran bildet die Abgrenzung zum Trägermaterial. Beide Membranen dienen zur Strömungsstabilisierung. Sie werden vor der Elektrophorese 12 h in dem jeweiligen Lösungsmittel aufbewahrt und bieten dann gegenüber Glasfritten[3] den Vorteil, daß sich der Widerstand nicht erhöht. Auf die obere Seite des Glasblocks setzt man die Trennsäule. Die gesamte Probenentnahmevorrichtung wird durch einen Flansch (zwei miteinander verschraubte Edelstrahlringe) zusammengehalten.

Trennsäule. Ihr Innendurchmesser und die Maße des Kühlmantels entsprechen denen des Zwischenstücks. Zum Packen der Trennsäule wird die Apparatur bis auf das obere Elektrodengefäß zusammengesetzt und mit Grundelektrolytlösung bis 1 cm über die Probenentnahmevorrichtung gefüllt. An den Membranen dürfen sich dabei keine

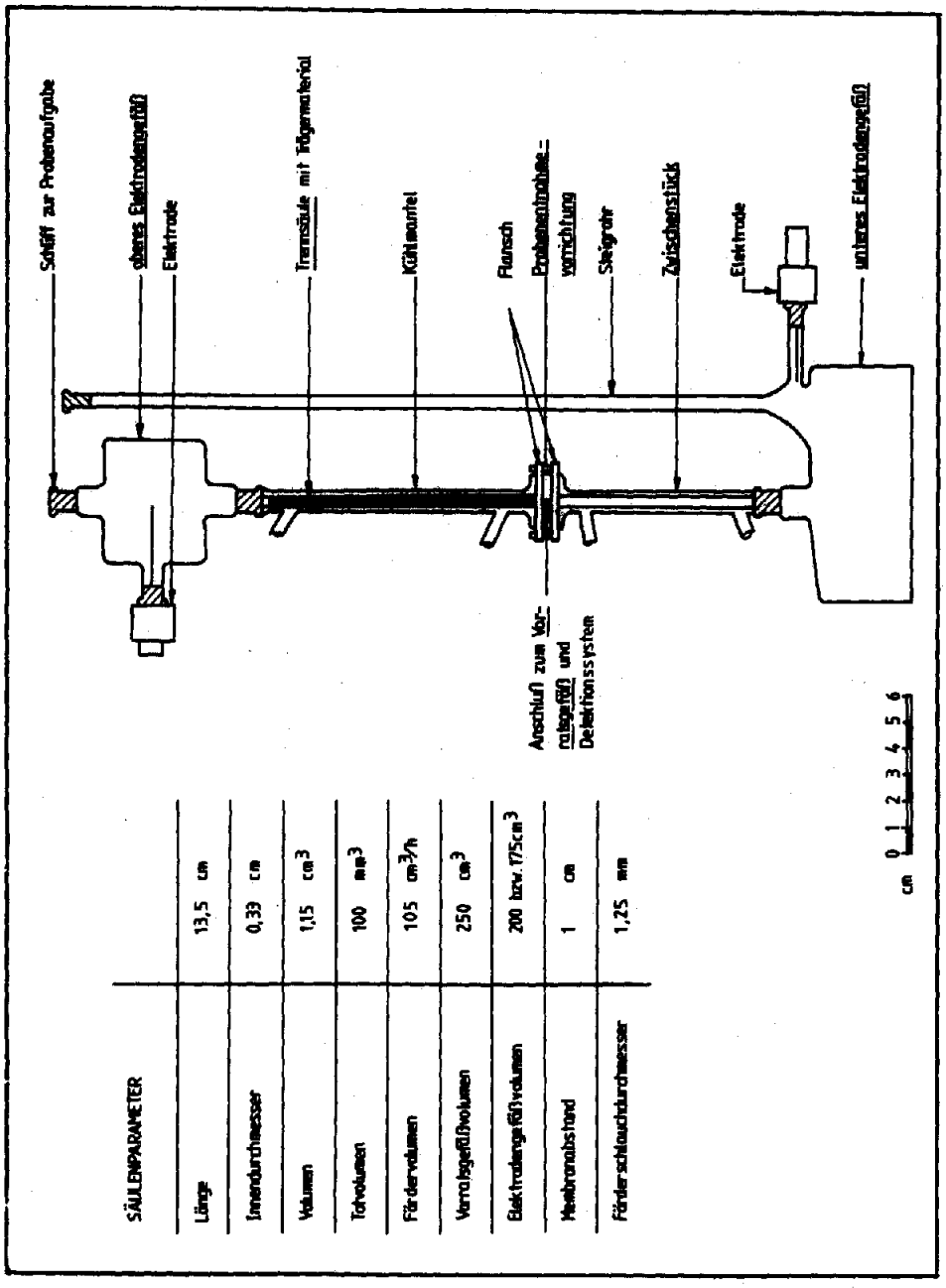

Abb. 1. Gesamtansicht der Apparatur.

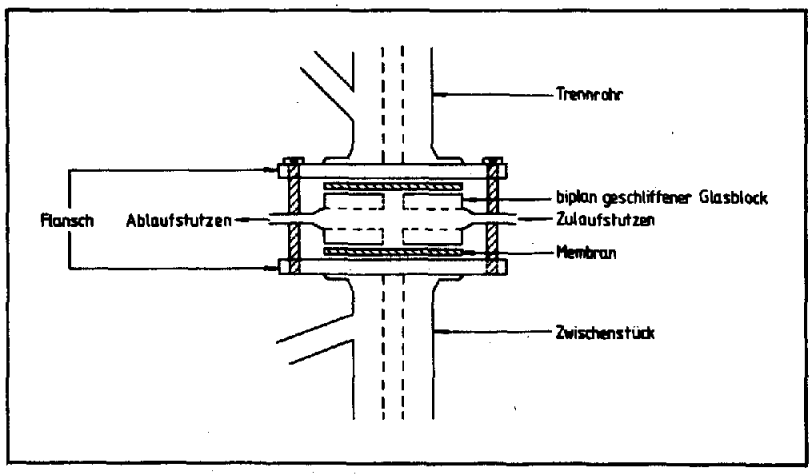

Abb. 2. Ausschnittvergrößerung der Probenentnahmevorrichtung.

Luftblasen befinden. Der Brei aus Trägermaterial und Grundelektrolyt wird anschließend langsam in die Säule eingeschlämmt. Diese muß vertikal stehen und darf während des Füllens nicht gekippt werden. Man läßt das Trägermaterial 12 h absetzen, bis eine konstante Höhe erreicht ist. Am oberen Ende der Trennsäule befindet sich ein Hohlschliff zur Aufnahme des oberen Elektrodengefäßes.

Oberes Elektrodengefäß. Es besitzt ein Volumen von 175 cm^3 und wird am unteren Schliff durch einen genormten Teflonschuh (NS 14.5) abgedichtet. Die Platinelektrode wird wie beim unteren Elektrodengefäß durch die seitliche Schliffhülse eingeführt. Über den oberen Schliff wird zunächst die Apparatur vollständig mit Grundelektrolytlösung gefüllt und dann die Probe mit einer Hamiltonspritze auf die Oberfläche des Trägermaterials aufgegeben. Der Schliff ist mit einem Stopfen abschließbar.

Vorratsgefäß. An einem Stativ auf der Grundplatte ist ein 250 cm^3 Scheidetrichter befestigt. Zwischen diesem Vorratsgefäß und dem Zulauf der Probenentnahmevorrichtung befindet sich eine Kühlschlange. Die Verbindungen erfolgen über Siliconschläuche (Abb. 3). Nach dem Zusammensetzen der Apparatur und Füllen wird das Vorratsgefäß auf Niveaugleichheit eingestellt.

Detektionssysteme

Die Detektion der aufgetrennten Substanzen kann visuell, diskontinuierlich nach Auffangen im Fraktionssammler bzw. kontinuierlich über eine Durchflußküvette erfolgen.

Hauptteile einer eigens entwickelten bis $-50°$ kühlbaren Durchflußküvette sind die Meßzelle mit den Zu- und Ablaufstutzen für die zu messende Probe, der Messingkühlblock mit den beiden Zuführungen für die

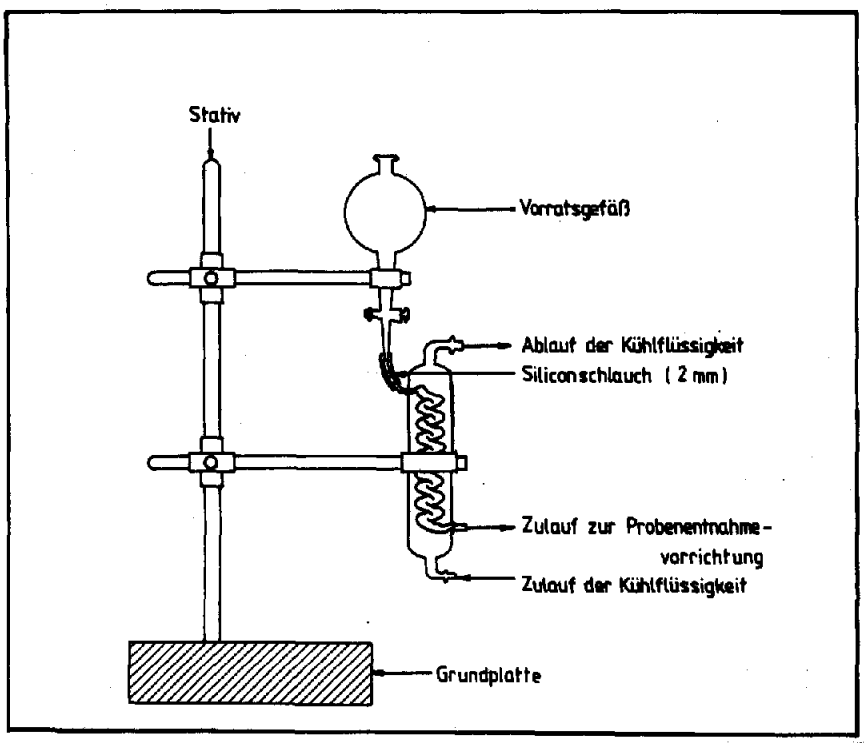

Abb. 3. Vorratsgefäß mit Kühlvorrichtung.

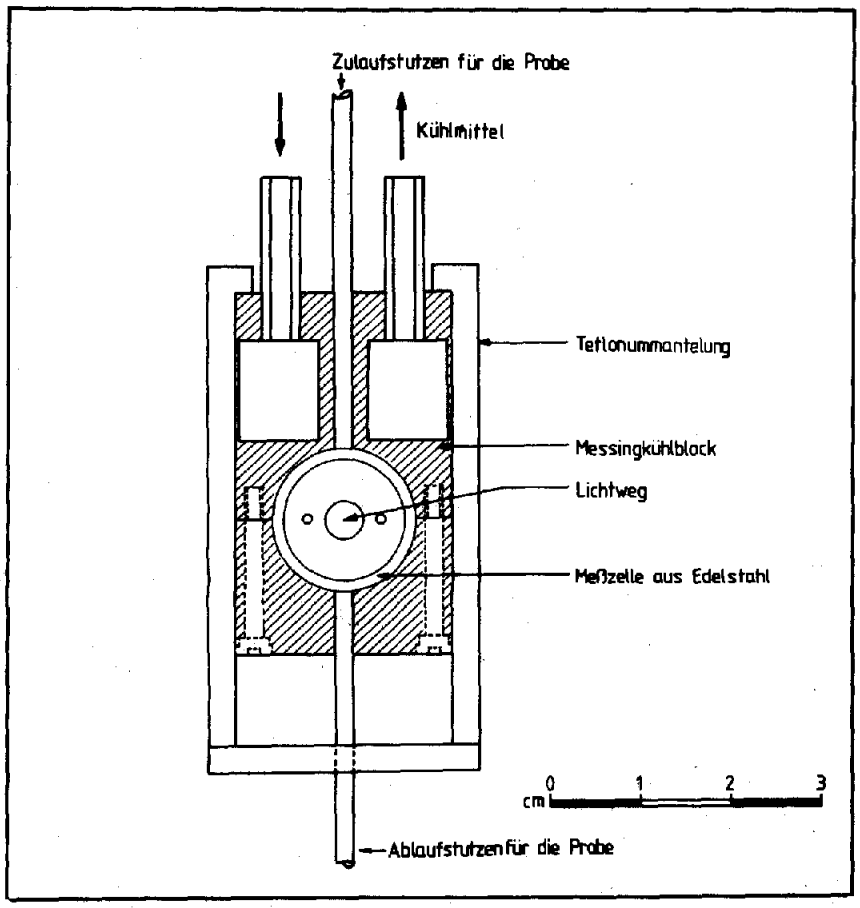

Abb. 4. Querschnitt durch die kühlbare Durchflußküvette senkrecht zum Lichtstrahl.

Kühlflüssigkeit aus dem Kryomaten sowie die Teflonummantelung (Abb. 4).

Die Meßzelle sitzt im unteren Teil eines gut kühlbaren Messingblocks. Dieser ist am oberen Ende ausgedreht und mit Stutzen für den Kühlkreislauf versehen. Der gesamte Kühlblock mit Meßzelle ist in ein zylindrisches Teflongefäß eingepaßt, dessen Maße so gewählt sind, daß die kühlbare Durchflußküvette gegen die normale käufliche Küvette des Spektralphotometers PM 2 D ausgewechselt werden kann.

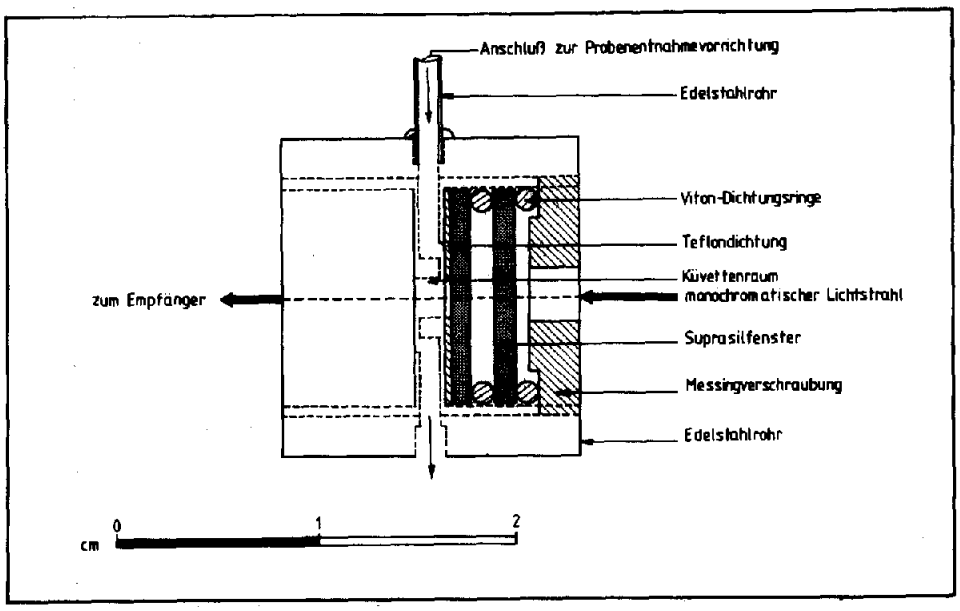

Abb. 5. Halbseitiger Schnitt durch die kühlbare Meßzelle parallel zum Lichtstrahl.

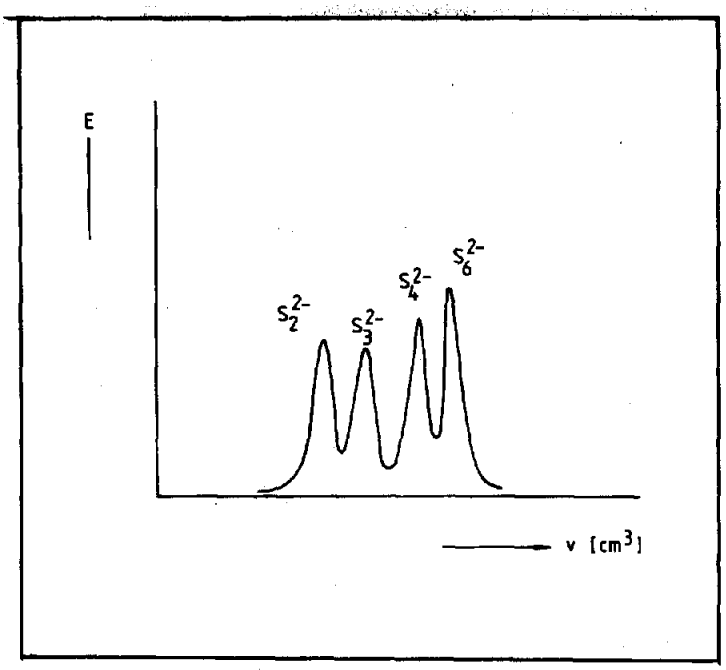

Abb. 6. Trennung von K_2K_2, K_2K_3, K_2K_4 und K_2K_6 in *N,N*-Dimethylformamid bei −50°C.

Meßzelle. Sie besteht aus einem Edelstahlrohr mit innen eingedrehtem Gewinde (Abb. 5) und ist durch einen 1 cm langen Siliconschlauch mit dem Ablaufstutzen der Probenentnahmevorrichtung verbunden.

Durchmesser und Länge der Meßzelle betragen jeweils 15 mm. In der mittleren massiven Edelstahlscheibe befinden sich eine zentrische Bohrung von 2 mm Durchmesser und vertikal dazu die Zu- und Ablaufbohrungen. Der eigentliche Küvettenraum (Zylinder von 2 mm Durchmesser und 2 mm Höhe) wird durch das beidseitige Auflegen der beiden inneren "Suprasil"-Fenster erhalten. Dazwischen befinden sich ringförmige Teflondichtungen. Zwei weitere "Suprasil"-Fenster bilden die äußere Begrenzung. Die gesamte Anordnung wird durch die Messingverschraubung und die "Viton"-Ringe zusammengepreßt. Die Strahlungsleistung bleibt aufgrund der doppelten "Suprasil"-Fenster bis −20° Kryomatentemperatur ungeschwächt. Die Verringerung der Durchlässigkeit durch Kondensatbildung und Vereisung beträgt bei −50° etwa 10%.

Kühlung. Vorratsgefäß, Trennsäule, Zwischenstück und Durchflußküvette kühlt man parallel über einen Kryomaten. Die Kühlschläuche sind durch Moosgummi weitgehend wärmeisoliert. Die Kühlung muß eine Stunde vor Beginn der Trennung eingeschaltet werden.

TRENNBEISPIELE

Die Anwendungsbreite der neuen Apparatur wird an drei Trennproblemen aufgezeigt. Diese stellen ausgewählte Beispiele für die Notwendigkeit des Einsatzes nichtwässriger Lösungsmittel dar. Folgende Trennungen werden durchgeführt:

(*a*) Kaliumpolysulfide als Beispiel für hydrolyseempfindliche Salze;

(*b*) Thiocyanato(phenylendiamin)chrom(III)-Komplexe als Beispiel für wasserschwerlösliche Salze;

(*c*) Aromatische Sulfonate als Beispiel für mit Kronenverbindungen komplexierte Salze.

Kaliumpolysulfide

Die Trennung eines Gemisches aus K_2S_2, K_2S_3, K_2S_4, und K_2S_6 in *N,N*-Dimethylformamid bei −50° ist in Abb. 6 wiedergegeben. In Tab. 1 sind die entsprechenden Trennbedingungen zusammengestellt.

Eine Trennung des Gemisches ist bei 0° nicht möglich. Bei dieser Temperatur stellen sich Gleich-

Tabelle 1. Trennbedingungen für die Trennung der Kaliumpolysulfide

Probegemisch:	Kaliumpolysulfidgemisch jeweils $10^{-2}M$ an K_2S_2, K_2S_3, K_2S_4, K_2S_6 (in *N,N*-Dimethylformamid)
Probevolumen:	50 µl
Spannung:	1000 V
Feldstärke	100 V/cm
Stromstärke:	8 mA
Trenntemperatur:	−50°C
Trennzeit:	2 h
Grundelektrolytsystem:	0,1*M* LiCl in *N,N*-Dimethylformamid
Träger:	Sephadex LH-20
Auswertung:	Extinktionsmessung in der Durchflußküvette bei 400 nm

Tabelle 2. Trennbedingungen für die Trennung der Thiocyanato(phenylendiamin)chrom(III)-Komplexe

Probegemisch:	0,125*M* Komplexgemisch bezogen auf Cr in Acetonitril
Probevolumen:	50 µl
Spannung:	1000 V
Feldstärke:	100 V/cm
Trenntemperatur:	0°C
Trennzeit:	1 h bei anodischen Komplexen 3 h bei kathodischen Komplexen
Grundelektrolytsystem:	0,1*M* KSCN in Acetonitril
Träger:	Al_2O_3
Auswertung:	Extinktionsmessung in der Durchflußküvette bei 540 nm

gewichte zwischen den einzelnen Polysulfidanionen und einem S_3^--Radikalionein.[4]

Thiocyanato(phenylendiamin)chrom(III)-Komplexe

Ein Gemisch aus Thiocyanato(phenylendiamin)-chrom(III)-Komplexen, hergestellt durch Umsetzung von $K_3[Cr(SCN)_6]$ mit *o*-Phenylendiamin in Acetonitril wird in Acetonitril in die vier möglichen Einzelkomponenten getrennt (Trennbedingungen in Tab. 2).

Ist die untere Elektrode als Anode geschaltet, erfolgt die Auftrennung in eine violette und eine rosa Zone, die nach ihren Wanderungsgeschwindigkeiten dem $[Cr(SCN)_6]^{3-}$ und dem $[Cr(SCN)_4(phen)]^-$ zugeordnet werden (Abb. 7 links). Im anderen Fall wandern zwei auf der Säule visuell nicht mehr erkennbare Zonen, die nach ihren Wanderungsgeschwindigkeiten dem $[Cr(phen)_3]^{3+}$ und dem $[Cr(SCN)_2(phen)_2]^+$ zugeordnet werden, zur Kathode (Abb. 7 rechts).

Auf diese art gelingt die Reindarstellung der einzelnen Komplexe.

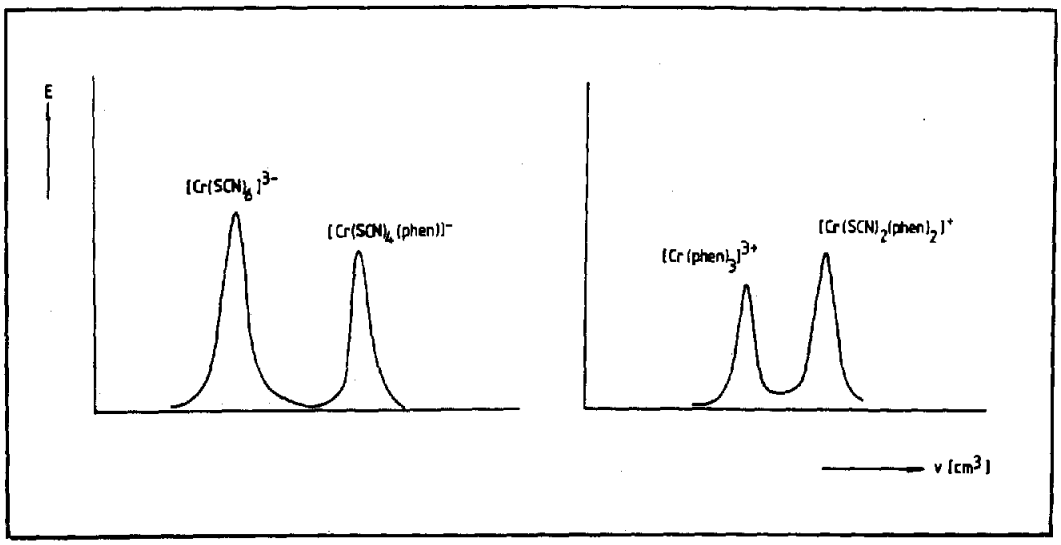

Abb. 7. Trennung von Thiocyanato(phenylendiamin)chrom(III)-Komplexen in Acetonitril.
Links: untere Elektrode als Anode.
Rechts: untere Elektrode als Kathode.

Tabelle 3. Trennbedingungen für die Trennungen der aromatischen Sulfonate

Probegemisch:	Gemisch 0,1*M* 2-Naphthol-6,8-disulfonat 0,1*M* 2-Naphthylamin-6,8-disulfonat bzw. 0,1*M* an DB-18-C-6 in Ameisensäure
Probevolumen:	50 µl
Spannung:	750 V
Feldstärke:	75 V/cm
Stromstärke:	40 mA
Trenntemperatur:	0°C
Trennzeit:	4 bzw. 2 h
Grundelektrolytsystem:	0,2*M* LiCl bzw. zusätzlich 0,1*M* an DB-18-C-6 in Ameisensäure
Träger:	Cellulosepulver
Auswertung:	Extinktionsmessung in der Durchflußküvette bei 335 nm

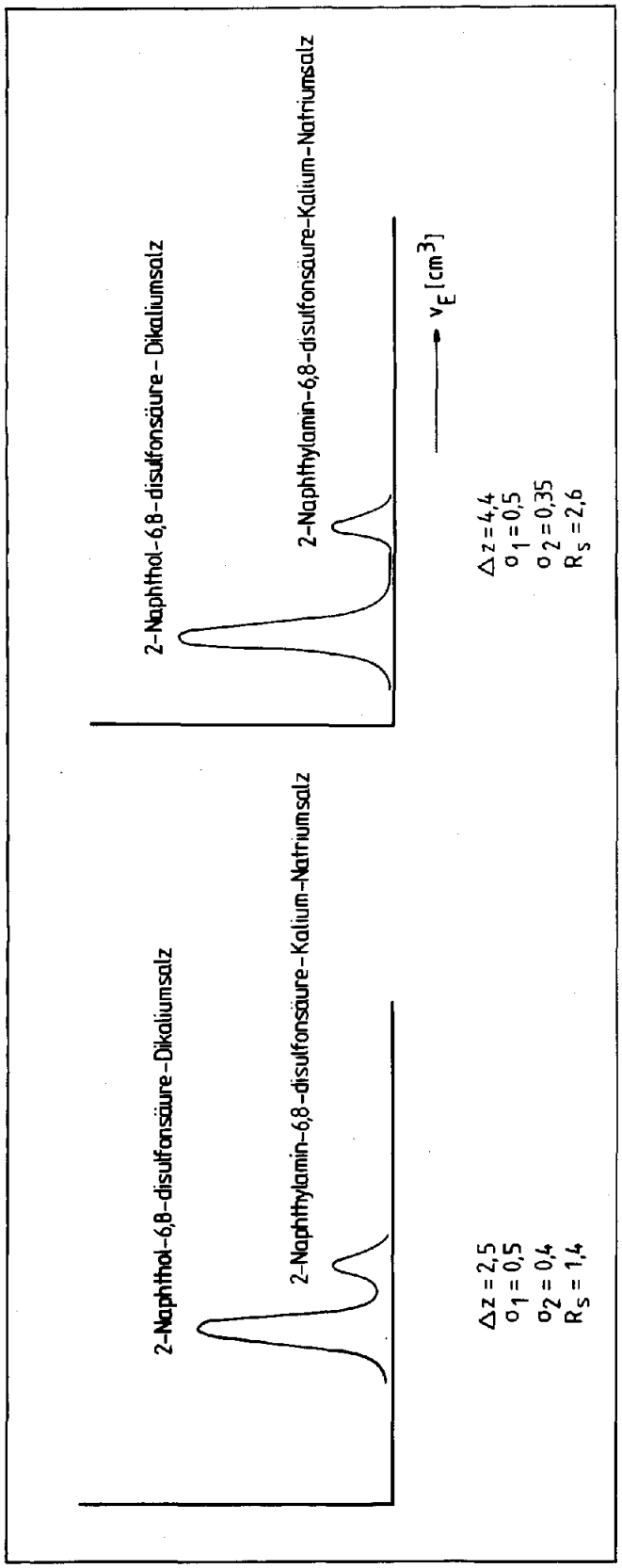

Abb. 8. Trennung von 2-Naphthol-6,8-disulfonsäure-Dikaliumsalz und 2-Naphthylamin-6,8-disulfonsäure-Kalium-Natriumsalz.
Links: ohne Zusatz von DB-18-C-6.
Rechts: mit Zusatz von DB-18-C-6.

Aromatische Sulfonate

Die Trennung chemisch sehr ähnlicher aromatischer Sulfonate stellt allgemein ein analytisches Problem dar. Die elektrophoretische Trennung in wässrigen Systemen wird durch die starke Hydratation der Ionen erschwert. Der Einsatz nichtwässriger Lösungsmittel bewirkt eine Verkleinerung der Solvathülle. Dadurch wird ein größerer relativer Unterschied in Radius und Masse der Ionen und damit der Ionenbeweglichkeiten erzielt. Jedoch bewirkt das organische Lösungsmittel Herabsetzung der Löslichkeit und Dissoziation der Salze. Diese Nachteile werden durch den Einsatz von Kronenverbindungen aufgehoben.

Mit Dibenzo-18-krone-6 wird die Trennung aromatischer Sulfonate, wie 2-Naphthol-6,8-disulfonat und 2-Naphthylamin-6,8-disulfonat, in Ameisensäure erheblich verbessert (Abb. 8). In Tab. 3 sind die Trennbedingungen zusammengestellt. Durch den Einsatz von Dibenzo-18-krone-6 erhöht sich der R_S-Wert[5] von 1,4 auf 2,6. Dies entspricht einer Verbesserung der Trenngüte von 85,7%.

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Summary—An apparatus for electrophoresis in non-aqueous solvents is described, which makes it possible to work in field strengths up to 150 V/cm and at temperatures down to −50°. A flow-through cell with two double "Suprasil" windows facilitates the photometric evaluation of the separations, and keeps the sample cool until it reaches the detection system. Potassium polysulphides have been separated as an example of salts sensitive to hydrolysis, thiocyanato(phenylenediamine)chromium(III) complexes as an example of salts only slightly soluble in water, and aromatic sulphonates as an example of salts complexed by crown compounds.

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A RAPID HIGH-PERFORMANCE ANALYTICAL PROCEDURE WITH SIMULTANEOUS VOLTAMMETRIC DETERMINATION OF TOXIC TRACE METALS IN URINE

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Summary—For the monitoring of toxic trace metals in urine a new high-performance trace analytical procedure with simultaneous voltammetric determination is presented. Particular emphasis has been placed on minimizing contamination by reducing the urine sample volume to 1 ml and consequently limiting the needed amount of $HNO_3/HClO_4$ and the duration (<20 min) of the wet digestion stage. The procedure consists of three stages. First 20 urine samples (1 ml each) are simultaneously freeze-dried overnight. They then require only a short wet digestion ($HClO_4/HNO_3$ 2:1, 20 min, 210°). They are then adjusted to pH 4.5 with acetate buffer and the trace metals are determined simultaneously by differential pulse anodic-stripping voltammetry at the mercury film electrode, the quartz digestion vessel being used as the voltammetric cell. If precipitates occur in the acidified samples, their trace metal content can be determined in the same manner, avoiding the low results commonly obtained by other methods. The procedure has high sensitivity with fair to good precision, covers a determination range from the sub-μg/l. to the medium μg/l. level and lends itself to automation. It is cheaper and more accurate than atomic absorption. Thus the procedure provides important potentialities for surveillance of occupationally exposed persons as well as for extended ecotoxicological baseline studies in man and cattle.

Man is widely exposed to toxic metals which are ingested by respiration and from food.[1–4] The degree of uptake depends on the local atmospheric toxic metal level and on the foods eaten. In addition there may be occupational exposure to still higher levels of toxic metals. Toxic metals are insidious, as they are biologically non-degradable but tend to accumulate in the vital organs of man, where they act progressively over extended time periods.[5] Fortunately a substantial fraction of the amount of toxic metals taken up is excreted. Because of the hazard constituted by toxic metals their monitoring in man is important in occupational medicine and toxicology, and is growing significant with respect to control of the toxic metal levels in the general population. Body fluids such as blood[6–8] and urine[9] are the most important types of sample from man and cattle, because of their ready availability and the possibility of contamination-free and reliable sampling (compared with that of such samples as hair[10]). Urine is especially convenient, and provides information on the level and rate of toxic metal excretion, as has been recently shown in studies on exposure to nickel.[11, 12]

Lead and cadmium are two of the very toxic metals deserving particular attention.[5] Their reliable and accurate determination at the low levels usually encountered in the urine of persons not occupationally exposed to them is a demanding task in trace analysis. Hitherto atomic-absorption spectroscopy (AAS)[13] has been the most popular method, frequently applied directly to the sample after pH adjustment or after digestion and extraction steps. At very low trace levels these procedures are especially liable to suffer from contamination and the general errors inherent in AAS with electrothermal excitation, as discussed elsewhere.[4, 14] Thus, to obtain meaningful data in the ultratrace range by electrothermal AAS requires expertise and experience, and also confirmation by an independent reliable trace-analysis procedure.[15–17]

Voltammetric methods, coupled with suitable digestion procedures, provide a very efficient and reliable alternative,[4, 6, 18, 19] combining extreme sensitivity with high accuracy and good precision. Furthermore, several trace metals can be determined in one run, in contrast to AAS which is essentially a sequential single-element method. The voltammetric instrumentation is also substantially cheaper.[4, 20]

Several authors have reported polarographic or voltammetric procedures for the determination of lead, cadmium and thallium in urine.[21–27] As found in our preliminary work and reported by previous

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authors,[22, 23] direct determinations after simple dilution and pH-adjustment are not dependable. Although they might work for some types of urine there is generally a significant risk of unreliable results owing to unexpected interferences from complexing surface-active substances frequently present in urine,[28, 29] making digestion of the sample mandatory. However, reported methods based on wet digestion suffer from high background levels of lead and cadmium originating from the glassware, making it virtually impossible to determine these elements at the low levels that are of interest in baseline studies on occupationally non-exposed persons.

The present paper describes a new voltammetric procedure applied after a rapid and efficient digestion of a freeze-dried sample. Some essentials of this approach have already been communicated in a brief preliminary note.[9] The procedure, outlined here in detail, is based on our extensive experience in the voltammetric determination of toxic trace metals in a variety of sample types ranging from various biomatrices,[4, 16, 18, 19] body fluids[6] and food,[4, 16, 18] to sea-water,[30] inland waters,[31] rain[32] and potable water.[33, 34] The voltammetric method used is differential pulse anodic-stripping voltammetry (DPASV) at the mercury film electrode (MFE).[18, 30] This type of electrode was first introduced into trace metal analysis by Florence.[35] Florence and Batley later came to the misleading conclusion that there was not much advantage in using it with DPASV.[36] However, the extraordinary sensitivity of this voltammetric method allows the volume of urine treated to be restricted to 1 ml, in contrast to the sample volumes generally used,[26] and makes possible the simultaneous and reliable determination of very low lead and cadmium levels in the urine. The procedure can also be extended to the simultaneous determination of several further toxic trace metals.

EXPERIMENTAL

Apparatus

Precleaned Eppendorf micropipettes (5–1000 μl) were used for taking sample aliquots and making standard additions. The urine samples (1 ml) were freeze-dried in thoroughly cleaned quartz cups in a Christ Beta I freeze-drier (Heraeus, Hanau, FRG).

The DPASV was performed with a PAR Polarographic Analyzer 174 A fitted with a Hewlett-Packard 700 B X–Y recorder, or a Metrohm Polarecord E 506 with the accessory BM 503. Use of the three-electrode technique and the potentiostats incorporated in the polarographs allows potentiostatic control throughout. The working electrode was a mercury film electrode on a glassy carbon carrier, of our own construction.[30] An Ingold saturated Ag/AgCl electrode connected to the cell by a salt bridge filled with 1*M* potassium chloride served as reference electrode and a coiled platinum wire was the auxiliary electrode. The solutions were deaerated prior to voltammetry by passing purified nitrogen (99.999%) through them for 10 min. During the voltammetry an inert atmosphere was maintained in the cell compartment by flushing nitrogen over the solution.

Reagents

Perchloric, nitric and acetic acids and sodium acetate were Merck "suprapur". Standard solutions of lead, cadmium and copper were Merck "Titrisol". Standard solutions of 0.4 μg/ml Pb + 0.4 μg/ml Cd and of 0.4 μg/ml Pb + 0.04 μg/ml Cd in 0.1*M* perchloric acid were used. The acetate buffer (0.5*M* acetic acid + 1*M* sodium acetate), which also serves as supporting electrolyte, was prepared from Merck "suprapur" reagents.

The water used for making the solutions was distilled five times in a quartz still, and triply distilled water was used for rinsing.

Procedure

Pipette 1 ml of the urine sample into a quartz cup and freeze-dry it with liquid nitrogen for 6–8 hr; 20 samples can be handled simultaneously in the Christ Beta I apparatus.

Wet digestion. Add 0.2 ml of conc. perchloric acid and 0.1 ml of conc. nitric acid to the dried sample, cover the quartz cup with a watch-glass and heat at 210° on a hotplate for 15–20 min. Evaporate almost to dryness to remove excess of acid. Dissolve the residue in 2–3 ml of fivefold distilled water. Cool to room temperature.

Voltammetric determination. Add 0.1 ml of 0.02*M* mercuric chloride for mercury film formation, 0.5 ml of acetate buffer to adjust to pH 4.5 and fivefold distilled water to give a total solution volume of 10 ml. Insert the quartz cup into the "Plexiglas" container. Deaerate with nitrogen for 10 min and begin formation of the mercury film. Perform the DPASV, evaluating the results by means of two standard additions.

RESULTS AND DISCUSSION

The general analytical procedure

Freeze-drying of the urine sample before digestion is essential, particularly for urine samples with very low levels of lead and cadmium. The amounts of concentrated acids required can then be restricted and the digestion time limited to less than 20 min. Wet digestion of 1 ml of the liquid urine sample would require five times as much acid and digestion for 60 min, resulting in greater contamination by lead and cadmium leached from the quartz cup. With preliminary freeze-drying the blank values can be reduced to $\leq$0.7 ng/ml for lead and $\leq$0.05 ng/ml for cadmium. These low blank levels are maintained throughout the procedure as the same quartz cup is used the whole time.

The freeze-drying admittedly takes time, but it can be performed for 20 samples simultaneously and arranged to go on overnight.

Several urine samples were found to give a precipitate on acidification. Because of adsorption and/or co-precipitation this contained a certain amount of trace metals. In such cases the precipitate is separated by centrifugation, washed with water, centrifuged again and then subjected to freeze-drying. In the subsequent wet digestion of the precipitate the same amount of acids as for 1 ml of clear urine is sufficient.

The voltammetric determination

The quartz cup used in the pretreatment steps serves as the cell for the voltammetric determination.

The solution from the digestion is spiked with mercuric chloride for formation of the mercury film electrode (MFE), adjusted to pH 4.5 and diluted to 10 ml to ensure immersion of all three electrodes when the quartz cup has been transferred into the "Plexiglas" container shown in Fig. 1. These operations should be performed under clean-bench conditions and as rapidly as possible to avoid contamination from the laboratory.

The MFE itself is formed each time during the initial phase of the voltammetry by the electrolytic deposition of Hg on the glassy carbon surface, from the sample solution. The glassy carbon manufactured by Tokai Mfg., Tokyo, is recommended. A rod of this glassy carbon, having a surface area of 0.28 cm^2, is sealed into a "Perspex" tube to give an electrode that can be rotated (Fig. 1). It resembles the electrode introduced by Sipos *et al.*[37] The polishing of the glassy carbon surface of freshly prepared electrodes and their treatment and storage, given in detail elsewhere,[30, 38] are important for satisfactory performance.

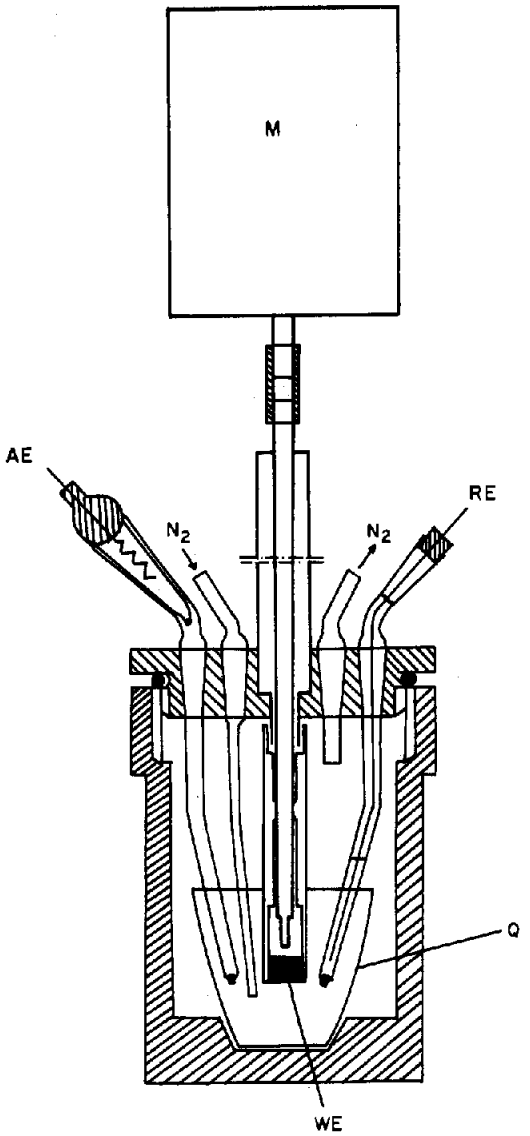

Fig. 1. Experimental arrangement for voltammetric determination. Q, quartz cup with sample, serving as voltammetric cell in "Plexiglas" container; WE, working electrode (MFE); AE, auxiliary electrode (Pt wire); RE, reference electrode with salt bridge; M, synchronous motor.

Here we describe only the treatment and application of an already activated glassy carbon carrier and its transformation into an MFE with a mercury film between 20 and 100 nm thick, which is most suitable for this trace analytical application.[39] In this study the method previously described for ultratrace determination of toxic metals in sea-water[30] was slightly modified.

During the deaeration period of about 10 min pure nitrogen is bubbled through the solution. At the same time the glassy carbon carrier is rotated by a synchronous motor at 1500 rpm and is polarized to a potential of −1.0 V. According to Štulíková,[40] at this potential the polished glassy carbon surface has a rather homogeneous distribution of active centres for deposition of mercury. The resulting homogeneous dense distribution of mercury microdroplets forms a well-adhering mercury film which grows in thickness with time, and the mercury film produced transforms the glassy carbon carrier into an electrode behaving like a mercury electrode. After this first film formation, serving to condition the glassy carbon surface, the potential is stepped to +1.0 V for 20 sec to strip off the first mercury film and any impurities.[38] The glassy carbon surface is then in activated condition and ready for analytical application.

With the electrode rotated at 1500 rpm to speed up mass transfer towards the interface, a cathodic deposition potential E_d of −1.0 V is applied for a deposition time t_d of 3 min. A fraction of the trace metals to be determined, lead and cadmium in this case, is reduced and deposited as amalgam in the growing mercury film (*in situ* formation of MFE). Thus from the very low bulk concentration of the trace metals a substantial electrolytic preconcentration in the small volume of the thin film is achieved.[6, 19] After 3 min the rotation and the passage of nitrogen are both stopped. To maintain an inert atmosphere nitrogen is now flushed through the "Plexiglas" container above the quartz cup. During the rest period t_r of 20 sec the solution comes to rest and mass transfer during the subsequent stripping stage is thus only by diffusion. At the beginning of t_r the potential is stepped to −0.8 V to save time in the following stripping stage, in which the potential is changed in a series of small rectangular pulses at 5 mV/sec to a value of +0.1 V, over a period of 2 min. The rectangular voltage pulses have a height of 50 mV, a duration t_p of 57 msec and a clock-time t_c of 0.5 sec. Because of this pulsed anodic polarization a fraction of the cadmium and lead amalgam is reoxidized, in the appropriate potential range, to the ionic state,[39] *i.e.*, stripped in the differential pulse

mode (DPASV). The whole sequence of DPASV is depicted schematically in Fig. 2*a*. The corresponding current peaks are the recorded signal (Fig. 2*b*). As usual in the version of differential pulse polarography common to the commercial instruments used,[41] only the current-difference between sampling intervals of 16.7 msec immediately before the beginning and the end of each pulse is recorded. In this manner the good signal-to-noise ratio inherent in the pulse polarographic mode originally developed by Barker and Gardner[42] is achieved, without interference by the charging current of the double-layer. The combination of this highly sensitive mode of pulse voltammetry with anodic stripping at an MFE is essentially the reason for the striking sensitivity and high performance of the method.

The recorded peak heights are proportional to the bulk concentrations of the corresponding trace metals in the sample solution. The actual peak heights are rather sensitive to traces of organic surface-active material which might still be present in the solution despite the digestion. These surfactants tend to be adsorbed at the electrode surface and thus affect the rate of the electrode process and consequently the corresponding current.[43] These risks prohibit the use of calibration curves for evaluation of the recorded current peaks. Therefore standard addition has to be used. An example is shown in Fig. 3*a*. Almost perfect regression lines are obtained and it has been established that two standard additions suffice for a reliable evaluation (Fig. 3*b*). In practice the evaluation was done with a programmable pocket calculator (Hewlett–Packard HP-55).

After the second standard addition the mercury film is wiped off with wet filter paper dusted with 0.05-μm abrasive powder and the fresh glassy carbon surface is rinsed with distilled water. It is then ready for the next sample, the first step again being formation of the mercury film during the initial deaeration phase.

If the electrode is not to be used again immediately it has to be kept with the glassy carbon surface immersed in mercury. It then remains in a state ready for further use without extensive polishing, even if it is stored for several weeks.[38]

The determination stage, including the initial 10 min of deaeration, takes less than 30 min for one sample, even at the ultratrace level. Because of the high sensitivity of DPASV the cathodic deposition time t_d can be restricted to as little as 3 min. The small t_d-values also have the great advantage that the concentrations of the amalgams formed remain below the levels at which interferences due to interactions such as intermetallic compound formation begin to play a role.[44] In conventional linear-scan anodic-stripping voltammetry such effects frequently require attention.

If desired, the total analysis time can be even further shortened to some extent by evaluating the results by a method applied in the analysis of large numbers of sea-water samples.[39] Use is made of the following relation for the amount of trace metal amalgam formed, W_{Hg}, which is proportional to the product of trace metal bulk concentration c and deposition time t_d.

$$W_{Hg} = \text{const. } ct_d \qquad (1)$$

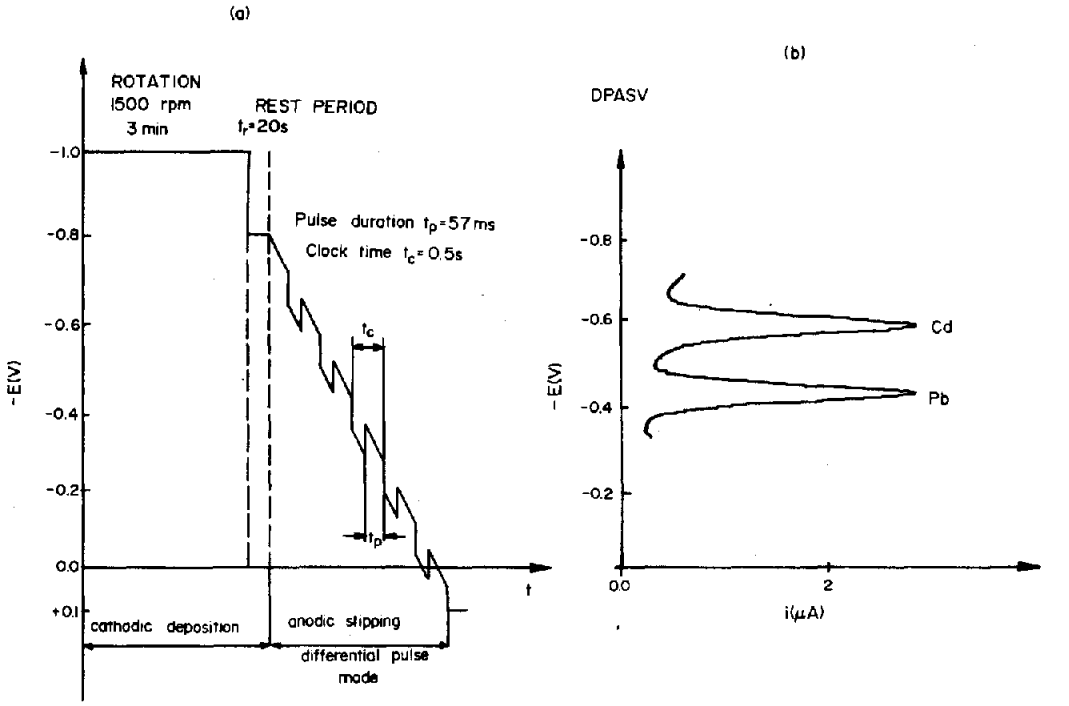

Fig. 2. (*a*) Principle of differential pulse anodic-stripping voltammetry (DPASV). (*b*) Example of resulting current–potential responses.

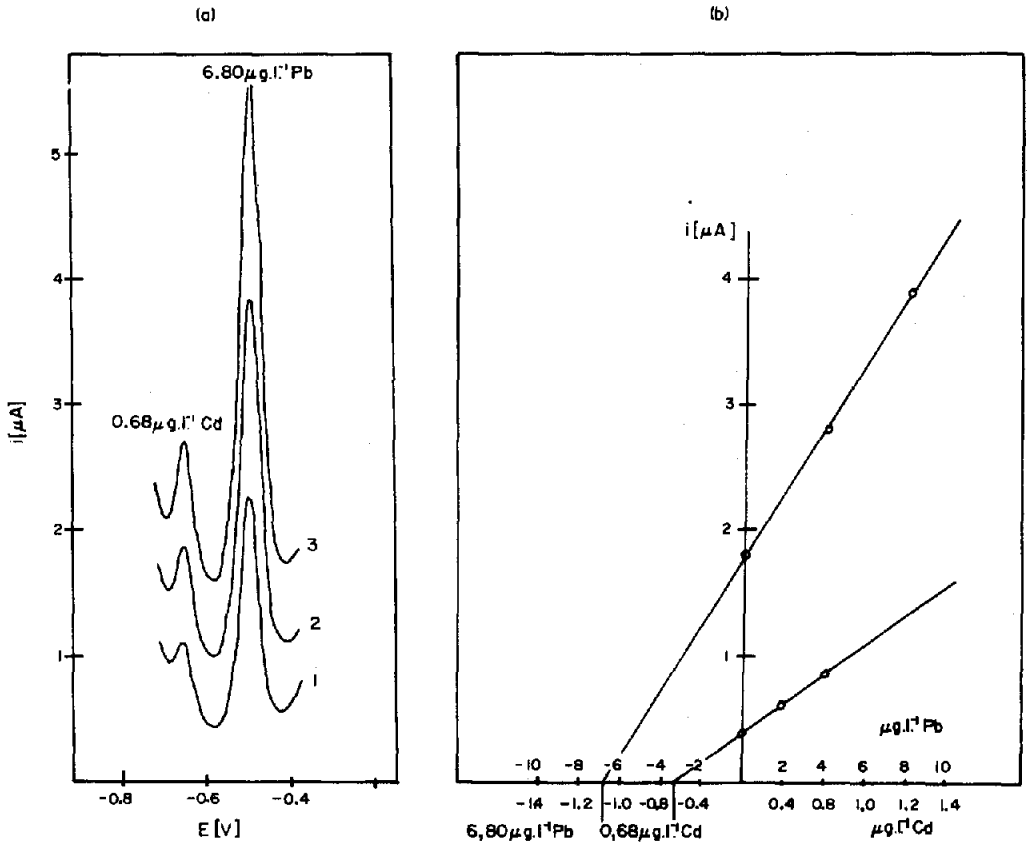

Fig. 3. (*a*) Example of simultaneous determination of Pb and Cd (1) and evaluation by two standard additions (2, 3): 0.025*M* acetic acid + 0.05*M* sodium acetate; t_d 3 min; E_d − 1.0 V. (*b*) Regression lines.

Consequently t_d can be decreased for each standard addition by the factor by which c increases. In this manner a further 1.5 min overall analysis time could have been saved for the example given in Fig. 3. This is rather a marginal saving, but one that will gain more significance if the method is adopted for large scale routine applications in analytical toxicology and if the determination stage is fully automated as has already been done for voltammetric on-line control of drinking water.[33]

Accuracy and precision

In accordance with the principle of using essentially independent trace analysis methods for testing accuracy,[15–17] now common in high-quality trace analysis, the results obtained by the new procedure were correlated with those obtained (with special precautions[45]) by electrothermal AAS after extraction of the trace metals with ammonium pyrrolidinedithiocarbamate and diethyldithiocarbamate (Figs. 4 and 5). The approximately 45° slope of the correlation lines and the values of 0.96 for the correlation coefficient confirm that the methods agree over the whole concentration range of interest down to $\leqslant 2$ μg/l. for Pb and $\leqslant 0.3$ μg/l. for Cd.

In this context the tendency of some urine samples to form precipitates on acidification, and the trace metal content in these precipitates, must be emphasized. Despite acidification to pH 2, up to 30% of the total lead and about 5% of the total cadmium is not released from the precipitate. Neglect of this effect may cause the results reported to be too low, particularly if the analysis is based on direct extraction of the trace metals from the urine sample.

The precision of the procedure described is reflected by the reproducibility obtained for two sets of 10 determinations on the urine of an occupationally exposed person (1) and a non-exposed person (2). The results are given in Table 1. The standard deviation is low for the higher levels of lead and cadmium in the urine of the exposed person and is low enough for surveillance purposes at the lower levels in the urine of the non-exposed person.

Extension to simultaneous determination of further toxic trace metals

The procedure can be extended to other toxic trace metals, as exploratory experiments with copper, zinc and thallium have demonstrated. If zinc is included, the cathodic deposition potential has to be adjusted to −1.2 V. Because of the limit set by the somewhat lower potential of hydrogen evolution at an MFE compared with a normal mercury electrode such as the hanging mercury drop electrode, the pH-adjust-

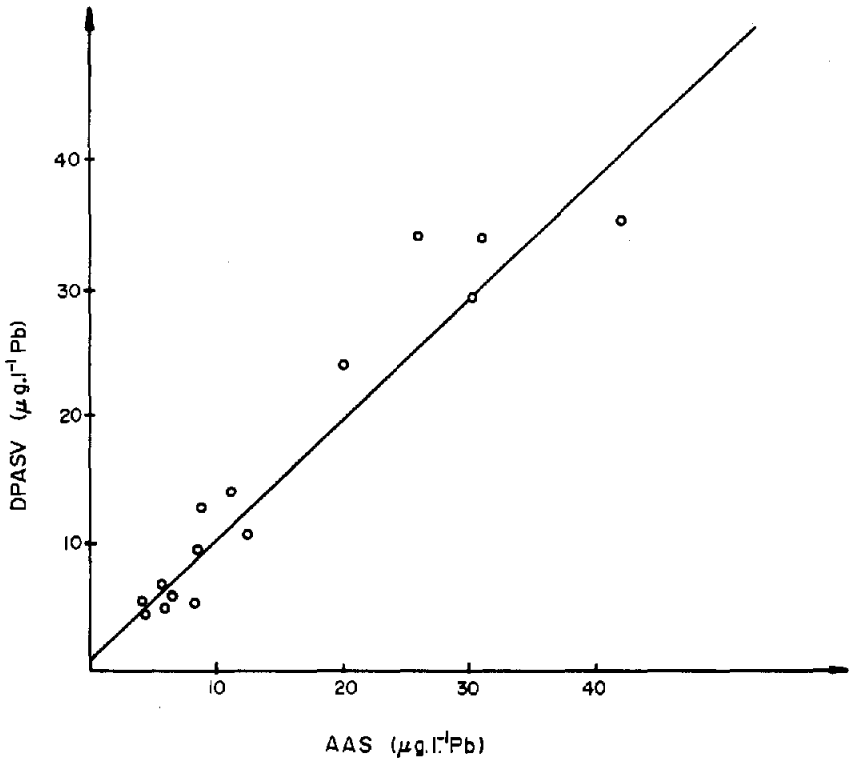

Fig. 4. Correlation between DPASV and electrothermal AAS determination of Pb in 15 urine samples: a_y 1.43; a_x −0.95; r 0.96; α 43°22′.

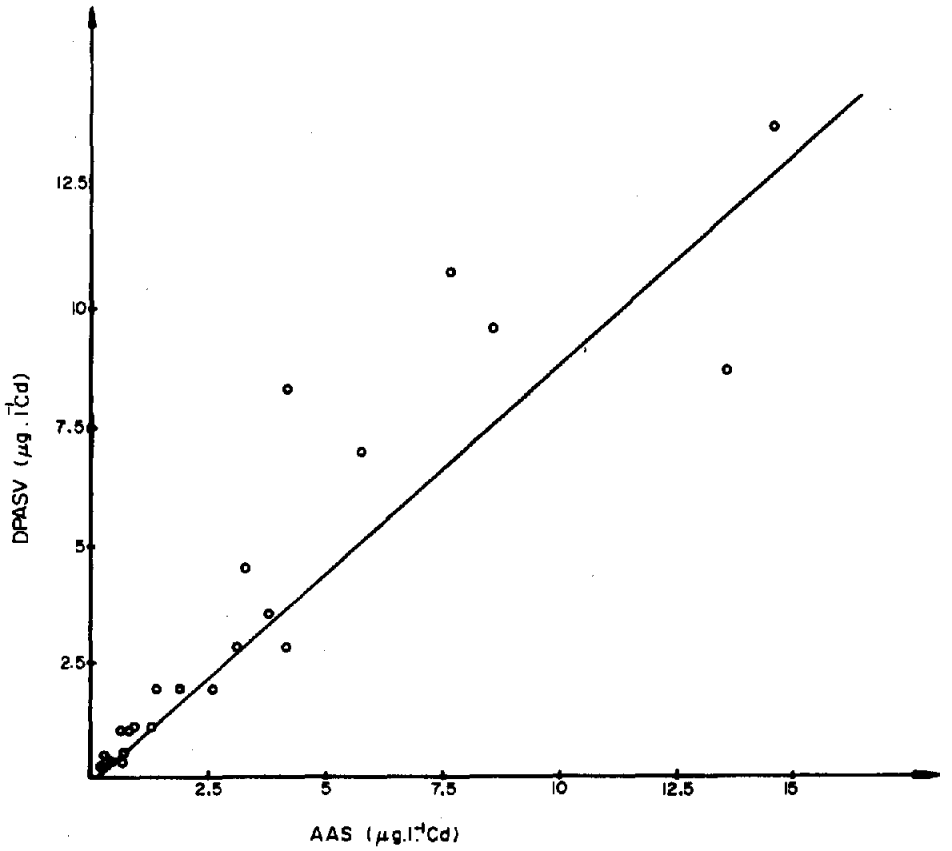

Fig. 5. Correlation between DPASV and electrothermal AAS determination of Cd in 22 urine samples: a_y −0.13; a_x 0.89; r 0.96; α 41°40′.

Table 1. Reproducibility of Cd and Pb determination in urine of exposed and non-exposed persons ($n = 10$, $P = 90\%$)

Metal	Exposed		Unexposed	
	$\bar{x} \pm ts$, µg/l.	RSD, %	$\bar{x} \pm$ ts, µg/l.	RSD, %
Cd	8.3 ± 0.8	±5.3	0.32 ± 0.25	±43
Pb	16.1 ± 2.1	±7.2	5.4 ± 1.0	±10.2

The standard deviation s was computed from the relation

$$s = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{(n-1)}}.$$

The Student–Fisher[48] coefficient t is 1.812 for the confidence interval $P = 90\%$ and $n = 10$.

The RSD-values are based on a confidence interval $P = 68.3\%$.

ment by the acetate buffer becomes somewhat more critical but remains feasible.

In the acetate buffer medium the peak for thallium coincides with that for cadmium at −0.65 V. However, thallium only rarely occurs in urine and therefore as a rule no interference with the determination of the commonly present cadmium is to be expected. In the exceptional cases when both are present, both metals can still be determined. First the sum of both is determined and then EDTA is added, which binds the cadmium in a strong and inert chelate not undergoing an electrode process at −0.65 V, leaving only the response corresponding to thallium. As any lead is also chelated by EDTA, its response disappears as well.

From our experience with the voltammetric determination of mercury with a twin gold-disc electrode by DPASV in the subtractive mode[16] in sea-water and (after photolytic decomposition of organic chelates by ultraviolet radiation) in rather polluted river water,[47] the development of a reliable voltammetric determination for mercury in urine also seems feasible.

Conclusion

This new procedure seems very promising for large-scale routine application in analytical toxicology and surveillance of trace metals in man and cattle. Owing to the sensitivity of DPASV the method covers the whole concentration range of interest from the ultra-trace levels in non-exposed persons, subjected only to ecotoxic pollution by certain heavy and less common metals, to the higher levels encountered in the urine of persons more or less occupationally exposed. The reliability is good, the rapidity satisfactory and the cost moderate, even for future automation.[49] A complete manually operated outfit including the voltammetric instrumentation and the equipment for sample pretreatment, will cost less than US $15,000. An electrothermal AAS outfit would cost at least twice as much.

Acknowledgement—The authors thank Ing. grad. Karin Brandt for the careful parallel analyses by electrothermal AAS. Financial support by the Federal Ministry of Research and Technology (BMFT), Bonn, in the framework of the project "Biocides and Environmental Chemicals" under contract MT 405g/AUT 03 is gratefully acknowledged. One of them (J.G.) thanks the Nuclear Research Centre (KFA), Jülich, for a grant during his attachment as guest scientist.

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SCHNELLTESTS ZUR LEISTUNGSFÄHIGKEIT VON BESTIMMUNGSVERFAHREN

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(*Eingegangen am* 4. *Oktober* 1978. *Angenommen am* 13. *Dezember* 1978)

Zusammenfassung—Für die Praxis brauchbare Bestimmungsverfahren setzen eine lineare Analysenfunktion in einem Zehnerpotenz-Arbeitsbereich voraus. Die Leistungsfähigkeit drückt sich in Verfahrens-Kenndaten wie Konstante der Analysenfunktion, Verfahrens-Standardabweichung und Bestimmungsgrenze unter anderen aus, die durch eine systematische Standardisierung ermittelt werden können. Es werden 3 einfache Tests auf Voraussetzungen zur Standardisierung sowie die Berechnung erster Schätzwerte der Verfahrens-Kenndaten beschrieben, wobei nur 2 Versuchsblöcke mit je 4 Untersuchungen erforderlich sind. Hierdurch können die Vorversuche zur Erstellung zuverlässiger Verfahren zielorientiert und mit geringem Versuchsaufwand durchgeführt werden.

Ein BESTIMMUNGSVERFAHREN (determination procedure) umfaßt eine detailliert beschriebene Arbeitstechnik mit weitgehend konstanten Arbeitsparametern zur quantitativen Erfassung der Portion eines bestimmten Stoffes in einem analytisch-chemischen Stoffsystem. Die Menge des Stoffes wird als BESTIMMUNGSPORTION (determination quantity) B bezeichnet, deren Quantität x_B in der Analytik mit den physikalischen Größen Stoffmenge n_B, Masse m_B oder Volumen V_B angegeben werden kann.

Wird ein Bestimmungsverfahren auf ein bestimmtes Untersuchungsobjekt angewandt, so nennt man die durch Probenahme und Probevorbehandlung erweiterte Arbeitsfolge ein ANALYSENVERFAHREN (analytical procedure) und die Menge des Untersuchungsobjektes für eine Einzelbestimmung eine ANALYSENPORTION (sample quantity) A, deren Quantität x_A durch die physikalischen Größen Stoffmenge n_A, Masse m_A oder Volumen V_A angegeben werden kann. Die Bestimmungsportion B ist in diesem Fall stets Teil der Analysenportion A. Aus den Verhältnissen der beiden Portionen folgen Gehaltsangaben (contents), wie Anteile (fractions) oder Konzentrationen (concentrations) unter anderem.

Die Leistungsfähigkeit eines Analysenverfahrens ist vor allem von der Leistungsfähigkeit des gewählten Bestimmungsverfahrens abhängig, deren wesentliche Kenndaten der Arbeitsbereich für Bestimmungsportionen x_0 bis x_u, die Verfahrens-Standardabweichung s_x, die Verfahrenskonstante V und ihr mittlerer Fehler s_V, die Bestimmungsgrenze x_G sowie Angaben zur Selektivität sind. Daher ist es zweckmäßig, Bestimmungsverfahren durch schematisierte Testuntersuchungen mit einer für alle Verfahren einheitlichen Vorgehensweise zu standardisieren, um vergleichbare Kenndaten zu erhalten. Hierüber wurde in einer Reihe von Arbeiten ausfürlich berichtet.[1–7]

Im Rahmen der Vorversuche zur Standardisierung können durch geeignete Versuchsplanung und Auswertung Schätzwerte für die Kenndaten erhalten werden, die mit einem Minimum an Versuchs- und Rechenaufwand erste Aussagen über Brauchbarkeit und Leistungsfähigkeit der gewählten Arbeits- und Meßtechnik ermöglichen und gegebenenfalls Anlaß zu einer gezielten Modifizierung der Vorgehensweise und der Arbeitsparameter sein können. Andererseits kann die nachfolgend beschriebene Testmethodik auch zu einer ersten Beurteilung von neuen Analysengeräten oder Laborpersonal eingesetzt werden. Wegen des geringen Umfanges der Versuche kann sie die eigentliche Standardisierung zwar nicht ersetzen, wohl aber eine erhebliche Verkürzung der Arbeiten im Vorfeld bewirken.

VERSUCHSPLANUNG, DURCHFÜHRUNG, AUSWERTUNG

Bei einer im eigenen Labor neu zu entwickelnden oder aus der Literatur entnommenen Bestimmungsmethodik ist zuerst der Arbeitsbereich festzulegen. Man wählt aus den bisher bekannten Daten einen Zehnerpotenzbereich der Bestimmungsportion mit einer oberen Grenze x_0 und einer unteren Grenze $x_u = 0{,}1x_0$ aus. In der Regel sollte dies ein "glatter" Zehnerpotenzbereich der Stoffmenge (amount of substance) mit der SI-Basiseinheit mole sein, mithin $(n_B)_0$ bis $(n_B)_u = 0{,}1(n_B)_0$, um von vornherein eine allgemeine Vergleichbarkeit verschiedener Bestimmungsverfahren zu gewährleisten. Nur in diesem Fall sollte von "Standard-Arbeitsbereichen" gesprochen werden.[1] Die nachfolgend beschriebene Testmethodik gilt jedoch universell für alle analytisch bestimmten Resultate x.

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Nach einer vorläufigen Arbeitsvorschrift werden in einem möglichst selektiv wirkenden analytisch-chemischen Grundsystem zwei Versuchsblöcke mit je 4 Parallelbestimmungen mit vorgegebenen Bestimmungsportionen an der oberen Grenze x_0 und der unteren Grenze $x_u = 0{,}1x_0$ des gewählten Arbeitsbereiches durchgeführt. Die erhaltenen analytischen Rohsignale S (Meßwerte) werden mit Hilfe der jeweils maßgebenden Signalfunktion in die Informationswerte I umgerechnet. Zu jedem Probewert I_x werden zusätzlich ein Leerwert I_L (nur Grundsystem) und gegebenenfalls auch ein Referenzwert I_R (Grundsystem plus Referenzzusatz) ermittelt und tabellarisch zusammengestellt. Reihenfolge der Datenermittlung ist:

$$I_L; I_x \quad \text{bzw.} \quad I_R; I_L; I_x$$

Diese erste Datentabelle wird durch Errechnung der endgültigen Informationswerte I aus den obigen Teil-Informationswerten nach

$$I = I_X - I_L \quad \text{bzw.} \quad I = \frac{I_X - I_L}{I_R - I_L} \tag{1}$$

und der als Empfindlichkeitsmaß anzusehenden Verhältnisse

$$K = \frac{x}{I} \tag{2}$$

vervollständigt. Die Vorgehensweise sei nachfolgend an zwei typischen Beispielen gezeigt.

Beispiel 1: *Spektralphotometrie in Lösungen*

Signalwerte S sind in der Spektralphotometrie vorzugsweise Durchlässigkeiten T(in %), die sich mit der einfachen Signalfunktion $E = -\log(T/100)$ in Informationswerte I in Form der Extinktion E umrechnen lassen.

Als praktisches Beispiel sind in Tabelle 1 die Daten zusammengestellt, die bei der Voruntersuchung einer spektralphotometrischen Phosphorbestimmung als P–V–Mo-Komplex für den Mikromole 2-Arbeitsbereich, entsprechend $x = n_B$: 100,0 bis 10,0 µmole, erhalten wurden.[6] Im vorliegenden Fall sind die relativ hohen Leerwerte E_L praktisch allein durch gelbe Eigenfärbung des als Reagenz verwendeten Vanadates bedingt.

Beispiel 2: *Röntgenfluoreszenzanalyse kleiner Elementmengen*

Signalwerte S sind in der RFA der Anzahl der innerhalb einer festgelegten Meßzeit Δt gemessenen Impulse. Die Signalfunktion ist mit $I = S/\Delta t$ sehr einfach. Wegen unvermeidlicher Meßdatenschwankungen arbeitet man mit einer variablen Referenznormierung.[2] Wird die Meßzeit Δt für alle Messungen konstant gehalten, so ist eine Umrechnung von S in I nicht erforderlich, da

$$I = \frac{I_X - I_L}{I_R - I_L} = \frac{S_X - S_L}{S_R - S_L}$$

ist. Als praktisches Beispiel sind in Tabelle 2 die Daten zusammengestellt, die bei der Voruntersuchung einer Spurenbestimmung für Eisen in Molybdänmaterial im Nanomole 3-Arbeitsbereich, entsprechend $x = n_B$: 1000 bis 100 nmole, erhalten wurden.[7] Die Referenznormierung wurde mit einer Referenzmenge $n_R = (n_B)_0 = 1000$ nmole Fe vorgenmommen. Als Analysenportion wurde eine Einwaage festgelegt, die $m_A = 1000$ mg Mo entspricht. In Form von Molybdat ist sie Bestandteil des analytisch-chemischen Grundsystems. Unter diesen Verhältnissen folgt mit M(Fe) = 55,84 ng/nmole ein Massen-Arbeitsbereich von m_B: 55,84 bis 5,58 µg Fe und mit $m_A = 1{,}000$ g ein Arbeitsbereich von 55,84 bis 5,58 µg/g (= ppm). Die oben beschriebene Referenznormierung mit $x_R = x_0$ (obere Bereichsgrenze) erweist sich als sehr zweckmäßig. Theoretisch sind bei einer Analysenfunktion $x = VI$ sodann Informationswerte von $I_0 = 1{,}00$ für x_0 bis $I_u = 0{,}10$ für x_u zu erwarten. Als Verhältnis müßte bei einwandfreien Verfahren $K = n_R$ gefunden werden. Größere Abweichungen von den theoretischen Daten weisen bereits hier auf erhebliche Mängel des Verfahrens hin.

Die Auswertung der Grunddaten erfolgt durch Bildung der Block-Kenndaten Mittelwert $\bar{y}_j$ und Standardabweichung s_j für die gefundenen Einzelwerte I

Tabelle 1. Spektralphotometrische Phosphorbestimmung—Grunddaten

Block Nr., j	Best. Nr., i	Portion n_B, µmole	Leerwert* E_L	Probewert* E_x	Inf. Wert† E	Verhältnis $K = n_B/E$, µmole
1	1	100,0	$0{,}052_0$	$1{,}199_0$	$1{,}147_0$	87,18
	2		$0{,}052_0$	$1{,}202_0$	$1{,}150_0$	86,96
	3		$0{,}053_0$	$1{,}200_0$	$1{,}147_0$	87,18
	4		$0{,}053_0$	$1{,}199_0$	$1{,}146_0$	87,26
2	5	10,0	$0{,}052_0$	$0{,}167_3$	$0{,}115_3$	86,73
	6		$0{,}052_0$	$0{,}167_3$	$0{,}115_3$	86,73
	7		$0{,}052_3$	$0{,}166_3$	$0{,}114_0$	87,72
	8		$0{,}051_7$	$0{,}166_3$	$0{,}114_6$	87,26

* Mittelwerte aus jeweils 3 Meßparallelen.
† Nach $E = E_x - E_L$.

Tabelle 2. Eisenbestimmung mit Röntgenfluoreszenzanalyse—Grunddaten

Block Nr., j	Best. Nr., i	Portion n_B, *nmole*	Ref. Wert* S_R, *Imp*	Leerwert* S_L, *Imp*	Probewert* S_x, *Imp*	Inf. Wert† I	Verhältnis $K = n_B/I$, *nmole*
1	1	1000	281050	20831	280833	0,9992	1000,8
	2		279280	21480	279389	1,0004	999,5
	3		283095	21147	274974	0,9690	1032,0
	4		282930	20218	281285	0,9937	1006,3
2	5	100	278577	20429	46596	0,0943	1059,9
	6		269662	20949	47839	0,1081	924,9
	7		266623	20476	47423	0,1095	913,5
	8		286218	21016	48442	0,1034	967,0

* Impulse für konstante Meßzeit $\Delta t = 40{,}0$ sec.
† Berechnet nach $I = (S_x - S_L)/(S_R - S_L)$..

und die Verhältnisse K nach:

$$\bar{y}_j = \tfrac{1}{4}\sum_1^4 y_i \quad \text{sowie} \quad s_j = \sqrt{\tfrac{1}{3}\sum_1^4 (y_i - \bar{y}_j)^2} \qquad (3)$$

Bei stark schwankenden oder sich gleichsinnig verändernden Daten innerhalb eines Blocks sollten Verläßlichkeitstests auf Ausreißer bzw. Trend durchgeführt werden.

Die Tabellen 3 und 4 bringen eine Zusammenstellung der errechneten Block-Kenndaten für die Beispiele 1 und 2.

TESTS AUF LEISTUNGSFÄHIGKEIT

Prüfung der Leerwerte

Der mittlere Probewert $\bar{I}_{x2}$ an der unteren Grenze eines Arbeitsbereiches sollte mindestens doppelt so groß wie das zugehörige Leerwertmittel $\bar{I}_{L2}$ sein. Die Schwankungen der Leerwerte, ausgedrückt als Variationskoeffizient $v_L = 1000 s_L/\bar{I}_L‰$, sollte eine bestimmte Größe nicht überschreiten. Diese Forderungen lassen sich durch folgende empirische Bedingungen ausdrückem:

$$\bar{I}_{x2}/\bar{I}_{L2} = \alpha \geqq 2$$

sowie

$$v_{L1} \text{ bzw. } v_{L2} \leqq 10.(\alpha - 1)\% \qquad (4)$$

Speziell für $\alpha = 2$ folgt v_{L1} bzw. $v_{L2} \leqq 10\%$.

Bei Nichterfüllung der Bedingungen (4) ist von vornherein ein wesentlicher Einfluß der Leerwertschwankungen auf die Verfahrens-Standardabweichung zu erwarten. Bei der Röntgenfluoreszenzanalyse und auch Aktivierungsanalyse unter anderem ist ein relativ hoher Leerwert durch den Untergrund nicht immer vermeidbar. So können zum Beispiel α-Werte von nur 1,1 resultieren. Die Auswirkungen auf die Verfahrens-Standardabweichungen sind dann aber gering, wenn zumindest die 2. Bedingung, hier mit v_{L1} bzw.

Tabelle 3. Spektralphotometrische Phosphorbestimmung—Blockdaten

Block Nr., j	Leerwerte	Probewerte	Verhältnisse
1	$\bar{E}_{L1} = 0{,}052_5$ $s_{L1} = 0{,}0005_8$	$\bar{E}_{x1} = 1{,}200_0$ $s_{x1} = 0{,}001_4$	$\bar{K}_1 = 87{,}1_3$ $s_{K1} = 0{,}13$
2	$\bar{E}_{L2} = 0{,}052_0$ $s_{L2} = 0{,}0002_5$	$\bar{E}_{x2} = 0{,}166_8$ $s_{x2} = 0{,}0005_8$	$\bar{K}_2 = 87{,}1_1$ $s_{K2} = 0{,}4_8$

Tabelle 4. Eisenbestimmung mit Röntgenfluoreszenzanalyse—Blockdaten

Block Nr., j	Referenzwerte	Leerwerte	Probewerte	Verhältnisse
1	$\bar{S}_{R1} = 281589$ $s_{R1} = 1797$	$\bar{S}_{L1} = 20919$ $s_{L1} = 5537$	$\bar{S}_{x1} = 279120$ $s_{x1} = 2880$	$\bar{K}_1 = 1009{,}7$ $s_{K1} = 15{,}2$
2	$\bar{S}_{R2} = 275270$ $s_{R2} = 8888$	$\bar{S}_{L2} = 21218$ $s_{L2} = 843$	$\bar{S}_{x2} = 47575$ $s_{x2} = 775$	$\bar{K}_2 = 966{,}3$ $s_{K2} = 66{,}5$

$v_{I,2} \leqq 1\%$, erfüllt wird (weitgehend konstanter Untergrund).

Sicherstellung der unteren Bereichsgrenze

Der Variationskoeffizient v_{x2} für Probewerte $\bar{I}_{x2}$ an der unteren Bereichsgrenze sollte höchstens zu 25% gefunden werden.

$$v_{x2} = 100 s_{x2}/\bar{I}_{x2} \leqq 25\% \qquad (5)$$

Bei Nichterfüllung von (5) liegt die Bestimmungsgrenze x_G oberhalb der unteren Bereichsgrenze x_u des gewählten Arbeitsbereiches, das heißt, der Arbeitsbereich kann mit dem Verfahren nicht vollständig erfaßt werden.

Prüfung auf Linearität

Einwandfreie Bestimmungsverfahren setzen eine Gerade durch den Nullpunkt, beschrieben durch die Analysenfunktion $x = VI$, zumindest in einem Zehnerpotenz-Arbeitsbereich voraus. Diese Bedingung kann für die Vorversuche als erfüllt angesehen werden, wenn zwischen den mittleren Verhältnissen $\bar{K}_1$ und $\bar{K}_2$ (erste Schätzwerte für V) ein Unterschied nicht feststellbar ist. Man bildet hierzu die Prüfgröße

$$PG = 2\left|\frac{K_1 - K_2}{\sqrt{s_{K_1}^2 + s_{K_2}^2}}\right| \qquad (6)$$

und vergleicht sie mit dem t-Wert der t-Verteilung für $P = 99\%$ statistischer Sicherheit (Signifikanzniveau $\alpha = 0{,}01$) und den Freiheitsgrad

$$f \simeq 5 \cdot \frac{(s_{K_1}^2 + s_{K_2}^2)^2}{s_{K_1}^4 + s_{K_2}^4} - 2 \qquad (7)$$

Die Formeln (6) und (7) beschreiben einen Spezialfall des elementaren Tests auf Unterschied von zwei Mittelwerten bei unterschiedlichen Standardabweichungen s_{K1} und s_{K2}. Als Grenzwerte des Freiheitsgrades findet man hier $f = 3$ für $s_{K1} \ll s_{K2}$ (häufig) bzw. formal $f = 8$ für $s_{K1} = s_{K2}$. Bei $f > 6$ ist jedoch stets $f = 6$ zu setzen. Für $f = 3$; 4; 5; 6 findet man aus t-Tabellen die Daten $t(99) = 5{,}84$; 4,60; 4,03; 3,71.

Bei $PG < t(99;f)$ ist ein Unterschied nicht feststellbar und es kann eine lineare Analysenfunktion $x = VI$ erwartet werden. Ob dies aber tatsächlich zutrifft, kann letztlich nur die vollständige Standardisierung entscheiden.

Testresultate bei den Beispielen

Beispiel 1

Mit den Daten der Tabelle 3 findet man:

nach (4)

$$\alpha = 0{,}1668/0{,}0520 = 3{,}21 > 2$$

sowie

$$v_{I,1} = 100 \cdot 0{,}00058/0{,}0525 = 1{,}10\% < 10 \cdot (3{,}21 - 1) = 22{,}1\%$$

$$v_{I,2} = 100 \cdot 0{,}00025/0{,}0520 = 0{,}48\% < 22{,}1\%$$

nach (5)

$$v_{x2} = 100 \cdot 0{,}00058/0{,}1668 = 0{,}35\% < 25\%$$

nach (6)

$$PG = 2\left|\frac{87{,}146 - 87{,}111}{\sqrt{0{,}131^2 + 0{,}477^2}}\right| = 0{,}146$$

$$f = 5\,\frac{(0{,}131^2 + 0{,}477^2)^2}{0{,}131^4 + 0{,}477^4} - 2 = 3{,}75 \rightarrow 4$$

und somit

$$PG < t(99;4) = 4{,}60$$

Danach werden alle Bedingungen erfüllt und das Bestimmungsverfahren ist zur Standardisierung geeignet.

Zweckmäßig werden in einer Abschlußtabelle zur Datenstruktur die vorgegebenen Daten x_B den mit der Analysenfunktion $x_B^* = VI$ gefundenen Daten gegenübergestellt, wobei auch die jeweiligen Einzelabweichungen $\Delta x_B = x_B - x_B^*$ sowie die Mittelwerte und Standardabweichungen für die zwei Blöcke aufzuführen sind.

Beispiel 2

Mit den Daten der Tabelle 4 findet man im zum Beispiel 1 analogen Rechengang:

nach (4)

$$\alpha = 2.24 > 2$$

sowie

$$v_{I,1} = 2{,}57\% < 12{,}4\%$$
$$v_{I,2} = 3{,}97\% < 12{,}4\%$$

nach (5)

$$v_{x2} = 1{,}63\% < 25\%$$

nach (6)

$$PG = 1{,}271 \quad \text{und} \quad f = 3{,}52 \rightarrow 4$$

und somit

$$PG < (99;\ 4) = 4{,}60$$

Auch dieses Bestimmungsverfahren erfüllt alle Bedingungen und ist zur Standardisierung geeignet.

SCHÄTZUNG DER VERFAHRENSKENNDATEN

Berechnung

Sofern die Bedingungen (4) bis (7) insgesamt erfüllt sind, kann eine erste Schätzung der Verfahrenskenndaten

V_x = Konstante der Analysenfunktion $x = VI$
s_x = Verfahrens-Standardabweichung
s_v = mittlerer Fehler der Konstanten V
x_G = Bestimmungsgrenze

für den gewählten Arbeitsbereich x_0 bis $x_u = 0{,}1x_0$ vorgenommen werden. Mathematisches Grundmodell hierzu ist bei Einhaltung des beschriebenen Versuchsplanes eine sehr einfache Ausgleichsrechnung. Man errechnet zunächst aus den jeweils 8 Einzeldaten die

Grundsummen:

$$S1 = \sum_1^8 I_i^2; \quad S2 = \sum_1^8 x_i I_i; \quad S3 = \sum_1^8 x_i^2 = 4{,}04 x_0^2 \tag{8}$$

und daraus unmittelbar die Kenndaten:

$$V_x = S2/S1 \tag{9}$$

$$s_x = \sqrt{\frac{1}{7}(S3 - V S2)} \text{ mit Freiheitsgrad } f = 7$$

$$s_V = s_x/\sqrt{S1}$$

$$x_G = \sqrt{2}\, t(99;7) s_x = 4{,}95 s_x$$

Bei PG $\geqq t(99; f)$ kann als Analysenfunktion eine Gerade mit konstantem Glied $x = U + VI$ oder eine gekrümmte Kurve vorliegen. Ein solcher Befund weist auf erhebliche Mängel in der chemischen Arbeitstechnik und/oder apparativen Meßtechnik hin und sollte nicht toleriert werden. Häufige Ursache für Geraden mit konstantem Glied U sind unzureichend ermittelte Leerwerte. Häufigste Ursache für gekrümmte Kurven sind Sättigungseffekte bei Bestimmungsportionen an der oberen Grenze des Arbeitsbereiches ($\overline{K}_1 > \overline{K}_2$), wodurch der Informationswertbereich "gestaucht" wird und zusätzlich ein "Pendeln" der Meßwerte bei wiederholter Messung auftreten kann.[1]

Werden eine oder mehrere der Bedingungen (4) bis (7) nicht erfüllt, so ist das getestete Verfahren wenig leistungsfähig und für die Praxis kaum brauchbar. Man sollte die Vorversuche unter Modifizierung von Arbeitsbereich, Arbeitsvorschrift oder des chemisch-analytischen Grundsystems wiederholen, bis alle Bedingungen erfüllt sind. Erst dann ist auch eine vollständige Standardisierung sinnvoll und erfolgversprechend.

Zusammenhänge

Die Verfahrenskonstante V besitzt die Dimension einer Bestimmungsportion pro Einheit des Informationswertes und ist damit ein Maß der Empfindlichkeit des Bestimmungsverfahrens. Je kleiner V gefunden wird, um so empfindlicher ist das Verfahren. Der mittlere Fehler s_V von V ist unmittelbar von der Verfahrens-Standardabweichung s_x abhängig, wie Gleichung (9) zeigt.

Die Verfahrens-Standardabweichung s_x ist eine universelle Maßzahl für Präzision und Richtigkeit des Bestimmungsverfahrens. s_x ist im Rahmen eines Zehnerpotenz-Arbeitsbereiches $x_0 = x_1$ bis $x_u = x_2 = 0{,}1 x_1$ eine konstante Größe, wodurch die Variationskoeffizienten im Bereich

$$v_0 = v_1 = 100 s_x/x_1\,\%$$

bis

$$v_u = v_2 = 100 s_x/x_2 = 10 v_1\,\% \tag{10}$$

veränderlich sind. Die Größe von s_x wird durch die zufälligen Abweichungen s_{x1} und s_{x2} innerhalb der zwei Blöcke und durch die Mittelwerte der systematischen Abweichungen $\overline{\Delta x_1}$ und $\overline{\Delta x_2}$ von gegebenen Daten x zu gefundenen Daten x^* bestimmt. Im vorliegenden Fall gilt der Zusammenhang

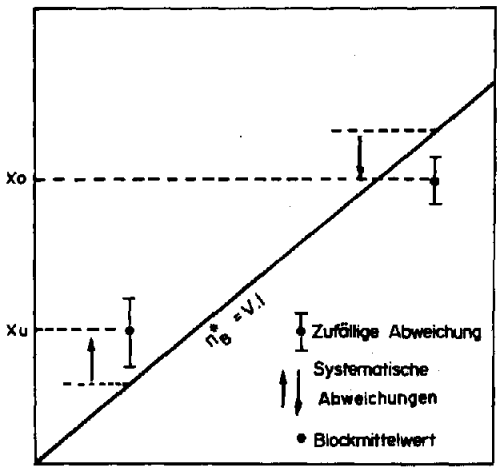

Abb. 1. Zufällige und systematische Abweichungen bei einer Ausgleichsgeraden

$$7 s_x^2 = 3(s_{x1}^2 + s_{x2}^2) + 4(\overline{\Delta x_1}^2 + \overline{\Delta x_2}^2) \tag{11}$$

Die häufig in der Literatur praktizierte Angabe nur der Block-Standardabweichungen s_{x1} und s_{x2} bzw. der Variationskoeffizienten v_1 und v_2 als Leistungskenngrößen eines Verfahrens ist nicht einwandfrei, da dies die oft erheblichen systematischen Abweichungen der Meßpunkte von der Ausgleichsgeraden nicht berücksichtigt, wie es Abbildung 1 schematisch verdeutlicht.

Theoretisch müßte die nach Gleichung (9) berechnete Abweichung s_x noch durch Multiplikation mit einem lageabhängigen Korrekturfaktor,

$$\beta = \sqrt{1 + \frac{1}{n} + \frac{(I_i - \bar{I})^2}{\sum_1^8 (I_i - \bar{I})^2}} \tag{12}$$

vergrößert werden. Mit $n = 8$ ergeben sich bei den vorliegenden Verhältnissen β-Werte um 1,12, die vernachlässigt werden können, zumal s_x hier nur ein erster Schätzwert ist.

Die Bestimmungsgrenze x_G ist die kleinste Bestimmungsportion in einem Bestimmungsverfahren, die sich noch signifikant ($P = 99\%$) von Null unterscheidet.[2] Sie ist daher unmittelbar von der Verfahrens-Standardabweichung s_x und ihrem Freiheitsgrad f abhängig, wie (9) zeigt. Bei $f = 7$ findet man $t(99) = 3{,}50$, so daß in diesem Fall der Variationskoeffizient an der Bestimmungsgrenze zu

$$v_G = 100 s_x/x_G = 100/(\sqrt{2} \cdot 3{,}50) = 20{,}2\% \tag{13}$$

erhalten wird. Bei vollständiger Standardisierung mit $6 \times 4 = 24$ Testuntersuchungen ergibt sich mit $f = 23$ und $t(99) = 2{,}807$: $v_G = 25{,}2\%$. Dieser v_G-Wert ist für die Bedingung (5) maßgebend. Bei n-facher Wiederholung von Grenzbestimmungen resultiert eine kleinere Mittelwertbestimmungsgrenze:

$$\bar{x}_G = x_G/\sqrt{n} \tag{14}$$

Tabelle 5. Spektralphotometrische Phosphorbestimmung—Datenstruktur

Block Nr., j	Best. Nr., i	Gegeben n_{Bi}, µmole	Gefunden n_{Bi}^{*}, µmole	Mittel $\bar{n}_{B}^{*}$, µmole	St.-Abw. s_j µmole	syst. Abweichungen Δn_{Bi}, µmole	$\overline{\Delta n_{Bi}}$, µmole
1	1	100,0	99.9_6	100,00	0.15_1	-0.0_4	± 0.0
	2	100,0	100.2_2			$+0.2_2$	
	3	100,0	99.9_6			-0.0_4	
	4	100,0	99.8_7			-0.1_3	
2	5	10,0	10,05	10.00_5	0.05_5	+0,05	$+0.00_5$
	6	10,0	10,05			+0,05	
	7	10,0	9,93			−0,07	
	8	10,0	9,99			−0,01	

Berechnet mit Analysenfunktion $n_{Bi}^{*} = 87.14_5 . E$.

Verfahrenskenndaten der Beispiele

Beispiel 1

Mit den Daten aus Tabelle 1 ergeben sich die Grundsummen:

$$S1 = (1{,}1470^2 + \ldots + 0{,}1146^2)$$
$$= 5{,}31975134$$
$$S2 = (100{,}0.1{,}1470 + \ldots 10{,}0 . 0{,}1146)$$
$$= 463{,}592$$
$$S3 = 4{,}04 . 100{,}0^2$$
$$= 40400$$

und daraus die Kenndaten:

$$V_n = 463{,}592/5{,}31975134$$
$$= 87{,}14542661 = 87{,}15\ \mu\text{mole}$$
$$s_n = \sqrt{\frac{1}{7}(40400 - V \cdot 463{,}592)}$$
$$= \sqrt{0{,}011055714} = 0{,}105\ \mu\text{mole}$$
$$s_{\bar{V}} = 0{,}105/\sqrt{5{,}319751} = 0{,}046\ \mu\text{mole}$$
$$n_G = 4{,}95 . 0{,}105 = 0{,}52\ \mu\text{mole}$$

Zur Vermeidung von erheblichen Rundungsfehlern sind die Rechengänge mit allen Stellen der Teilresultate durchzuführen und erst das Endresultat ist sinnvoll zu runden.

Tabelle 5 bringt die Abschlußtabelle zur Datenstruktur. Zum Vergleich seien die bei vollständiger Standardisierung gefundenen Daten[6] genannt:

$V_n = 86{,}99\ \mu$mole; $s_n = 0{,}138\ \mu$mole;

$s_{\bar{V}} = 0{,}040\ \mu$mole; $n_G = 0{,}55\ \mu$mole.

Beispiel 2

Mit den Daten der Tabelle 2 findet man im zum Beispiel 1 analogen Rechengang:
$S1 = 3{,}96886140$; $S2 = 4003{,}83$; $S3 = 4040000$
und daraus die Kenndaten:

$V_n = 1008{,}81$ nmole; $s_n = 11{,}3$ nmole:

$s_{\bar{V}} = 5{,}77$ nmole; $n_G = 55{,}9$ nmole.

Tabelle 6 bringt die Abschlußtabelle zur Datenstruktur. Zum Vergleich seien die bei vollständiger Standardisierung gefundenen Daten[7] genannt:

$V_n = 997{,}34$ nmole; $s_n = 8{,}3$ nmole;

$s_{\bar{V}} = 2{,}8$ nmole; $n_G = 32{,}7$ nmole.

Unterschiede der V_n-Werte zum Sollwert $[V] = n_B = 1000$ nmole sind nach dem Sollwert-*t*-

Tabelle 6. Eisenbestimmung mit Röntgenfluoreszenzanalyse—Datenstruktur

Block Nr., j	Best. Nr., i	Gegeben n_{Bi}, nmole	Gefunden n_{Bi}^{*}, nmole	Mittel $\bar{n}_{B}^{*}$, nmole	St.-Abw. s_j, nmole	Syst. Abweichungen Δn_{Bi}, nmole	$\overline{\Delta n_{Bi}}$, nmole
1	1	1000	1008,0	999,3	14,8	+8,0	−0,7
	2	1000	1009,2			+9,2	
	3	1000	977,5			−22,5	
	4	1000	1002,5			+2,6	
2	5	100	95,1	104,7	6,9	−4,9	+4,7
	6	100	109,1			+9,1	
	7	100	110,5			+10,5	
	8	100	104,3			+4,3	

Berechnet mit Analysenfunktion $n_{Bi}^{*} = 1008{,}8 . I$.

Test nicht feststellbar, so daß das Verfahren auch in dieser Hinsicht einwandfrei ist.

LITERATUR

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5. V—Gravimetrische Bestimmungen, *ibid.*, 1976, **280**, 205.
6. VI—Spektralphotometrie in Lösungen, *ibid.*, 1976, **282**, 1.
7. VII—Röntgenfluoreszenzanalyse kleiner Elementmengen, *ibid.*, 1977, **285**, 199.

Summary—Linear analytical functions covering at least a working range of one power of ten are the basis for useful determination procedures. The efficiency of the procedure is given by characteristic data such as constant magnitude of the analytical function, the standard deviation of the procedure and the determination limit. These can be evaluated by systematic standardization. Three simple tests are described to check the possibility of standardization, and a method is given for estimating values of the characteristic data, which requires only 2 sets of 4 experiments each. Thus preliminary work in the development of reliable procedures can be carried out purposefully, with only a few experiments.

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SURFACE AND THIN-FILM ANALYSIS: CONCEPTS, CAPABILITIES AND LIMITATIONS

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Summary—A brief survey of the concepts and limiting conditions of instrumental surface-analysis techniques and their use for in-depth distribution analysis of thin films is presented. The basic differences between the most important methods: Photoelectron Spectroscopy (ESCA), Auger Electron Spectroscopy (AES), Secondary-Ion Mass-Spectrometry (SIMS) and Ion-Scattering Spectrometry (ISS) are outlined. Examples of compositional profiles obtained in combination with sputtering illustrate the influence of information depth and of bombardment-induced micro-roughening on the accuracy of in-depth analysis.

The importance of surface and thin-film analysis in the development of new materials results from the dependence of many properties on interfacial composition. This is recognized for phenomena such as recrystallization, fracture, cohesion in composite materials, catalysis, corrosion, friction and wear, to mention only a few examples. It is therefore not surprising that with the aid of the developments in electronics and vacuum technique powerful physical methods of surface analysis[1] have been developed in the past 5–10 years to meet the demand.

To illustrate the significance of these modern physical or instrumental methods, Fig. 1 shows schematically the various steps in classical microchemical analysis.[2] These steps from preparation to determination can be clearly separated into a sequence of different operations often performed with different apparatus. In instrumental "*in situ*" analysis all these steps are combined into one. The main advantages of fast data acquisition and of suppression of the influence of the experimental environment are, however, somewhat outweighed by the complexity and entanglement of all stages on the atomic scale, where the details of the processes involved are not yet really understood.[3] These processes tend to alter the material under investigation itself and therefore pose ultimate limits in reliability.

Nevertheless the potential applications of surface analysis are so wide-reaching that it will have enormous influence in almost all branches of chemical analysis in the near future.[4] To give an outline of these challenging tasks, the concepts, capabilities and limitations of the present surface analysis techniques will be briefly discussed.

The reason why surface analysis and thin-film analysis are used in conjunction is two-fold. First, many of the surface-analysis methods obtain information not only from the outermost atomic layer of a solid (which is the physically defined surface) but also from deeper layers, so that a precise distinction can hardly be made. Secondly, since the surface specificity of a method is a requirement for high-resolution thin-film analysis, the latter is generally performed with a surface-analysis method.

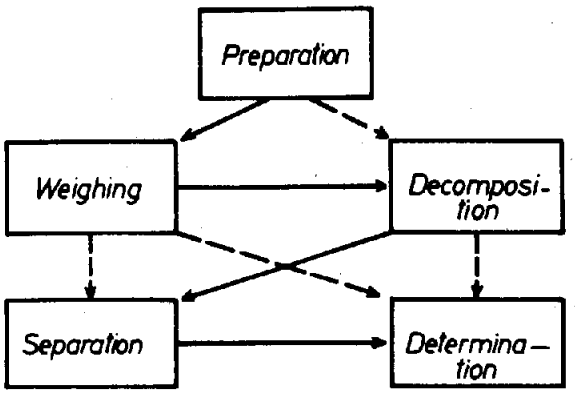


Fig. 1. Steps in microchemical analysis. After G. Tölg[2] (by permission of Elsevier Publishing Co. Ltd.).

SURFACE ANALYSIS METHODS

Basic concepts

All instrumental "*in situ*" surface-analysis methods are, in a rather general sense, probe methods.[1] That means that a solid is excited by some kind of energy and subsequently its response is observed by an appropriate technique.[5] Figure 2 is one of the usual representations of the fundamentals of surface-analysis techniques. If a beam of photons, electrons, ions or neutral particles or an electric field is applied, the solid can respond by emission of photons, electrons, ions and neutral species.

Detection of the secondary particles from the sample results in basically destructive methods (*e.g.*, SIMS), whereas detection of scattered primary particles, photons and electrons is basically non-destructive (*e.g.*, ESCA, AES, ISS). The term "basically" means that the amount of damage produced in the solid also depends on the excitation conditions, and may be considerable even for electron and photon beams.

Excitation by	Emission and Analysis of		
	Photons	Electrons	Ions (Neutrals)
Photons	XRF LOES LS IRS	ESCA (XPS) UPS (XAES)	(PD)
Electrons	EMP (APS) (CL)	AES LEED	ESD (EID)
Ions	IIX (PIX) SCANIIR (GDOS)	INS (IAES)	SIMS (GDMS) ISS RBS
Electric Field		FEM	FIM-AP

Fig. 2. Classification matrix for surface analysis techniques. XRF, X-ray fluorescence analysis; LOES, laser optical-emission spectroscopy; LS, light (Raman) scattering spectroscopy; IRS, infrared spectroscopy; ESCA, electron spectroscopy for chemical analysis (= XPS, X-ray-induced photoelectron spectroscopy; UPS, ultraviolet photoelectron spectroscopy; XAES, X-ray-induced Auger electron spectroscopy; PD, photodesorption; EMP, electron microprobe (X-ray) analysis; APS, appearance-potential spectroscopy; CL, cathodoluminescence; AES, Auger-electron spectroscopy; LEED, low-energy electron diffraction; ESD, electron-stimulated desorption (= EID, electron-induced desorption); IIX, ion-induced X-ray spectroscopy (⇒ PIX, proton-induced X-ray spectroscopy); SCANIIR, surface composition by analysis of neutral-species and ion-impact radiation; GDOS, glow-discharge optical spectroscopy; INS, ion-neutralization spectroscopy; IAES, ion-induced Auger-electron spectroscopy; SIMS, secondary-ion mass-spectrometry; GDMS, glow-discharge mass-spectrometry (= SNMS, sputtered neutral species mass-spectrometry); ISS, ion-scattering spectroscopy (= LEIS, low-energy ion-scattering spectroscopy); RBS, Rutherford back-scattering spectroscopy (= HEIS, high-energy ion-scattering spectroscopy); FEM, field-electron microscopy; FIM-AP, atom-probe field-ion microscopy.

Capabilities and limitations

To check the applicability of any of the principles outlined we have to compare its features with the requirements of an elemental surface analysis.

In the optimum case we will expect:

(1) information over depths in the monolayer range
(2) detection of all elements
  (*a*) quantitatively
  (*b*) with high sensitivity
  (*c*) with negligible matrix effect
(3) practicable experimental conditions.

Some techniques also possess useful additional features such as isotope detection or ability to obtain chemical information.

Surface-analysis methods have to be chosen according to their ability to reach these goals.

Applying the principles stated above to the different excitation and emission species in the form of a classification matrix[5–7] we see that only a few of the 60 or so possible methods[7] are suited for practical surface analysis. The most prominent are ESCA (photoelectron spectroscopy), AES (Auger-electron spectroscopy), SIMS (secondary-ion mass-spectrometry) and ISS (ion-scattering spectrometry) (Fig. 2). [The field-ion microscopy atom-probe[8] (FIM-AP) is a unique technique allowing three-dimensional resolution on the atomic scale, but it is too heavily restricted to special samples and experimental conditions to be a universally applicable surface-analysis technique.] Figure 3 shows the surface specificity of the methods mentioned, in terms of depth resolution and lateral resolution. Note that EMP (electron microprobe) gives depth resolution far beyond that of the other techniques indicated. Table 1 shows a compilation of the most relevant information on the capabilities of the methods. The numbers given should be taken only as a rough guide.

The lateral resolution depends mainly on the possibility of generation of a highly focused excitation beam with useful intensity. This is feasible for high-energy charged particles, such as electrons and ions (AES, SIMS), but not for X-rays (ESCA). The depth to which any method can penetrate to give information (the information depth) depends on the escape depth of the detected species. In this respect the most surface-specific method is ISS, because here it is not secondary particles, but only the energy loss of the primary ions scattered from the uppermost atomic layer that is detected.[9] In SIMS the information depth is mainly confined to the first atomic layer, but with higher energy-transfer from the primary ions deeper layers can also contribute to the output signal.[5,10,11]

In the secondary-electron detection methods, ESCA and AES, the escape probability of energetic electrons is the determining parameter for the information depth, their mean range being between 2 and 10 monolayers (about 0.4–2 nm) in most materials.[12,13] This point is considered below in more detail.

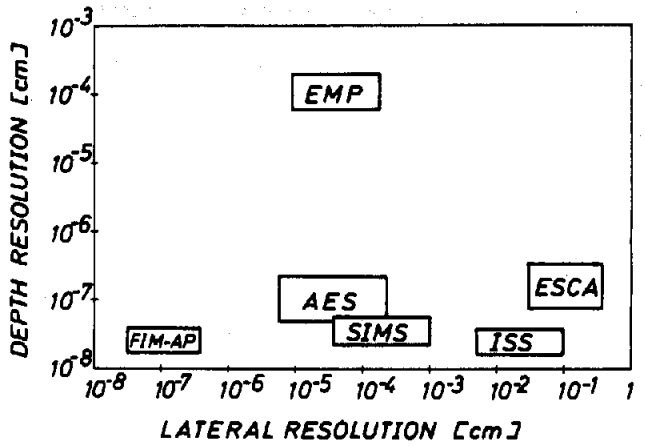


Fig. 3. Typical values of depth resolution and lateral resolution of surface-analysis techniques (for abbreviations see Fig. 2).

The detection sensitivity of all energy-analysing methods (ISS, ESCA, AES) is principally limited by an appreciable background due to random energy-loss by the secondary particles. This is not the case in mass-detection methods (SIMS), where we can obtain very high sensitivities suitable for direct trace analysis even below the ppm range. This unique feature of SIMS is, however, somewhat outweighed by the large differences in relative sensitivity between the elements, covering several orders of magnitude.[10] The complicated ion-emission process leads to a large variation in the output, depending on the matrix and the ion-species detected.[5,10,11] Absolute quantification in SIMS is a difficult task, because the raw data give only a very distorted view of the composition of a surface layer, although great progress has been made in recent years by the use of reactive species as primary ions, for instance oxygen ions.[10] For quantification, the lower sensitivity differences and almost negligible matrix effects in ESCA and AES are much more favourable.[14,15]

In qualitative elemental analysis, another unique feature of SIMS is its ability to detect hydrogen, which is not detected by the other methods. Isotopes can be detected with SIMS and to a more limited extent by ISS.

Chemical information is unambiguously obtained only by ESCA, since here the binding energy is directly observed.[14,15] ISS provides no chemical information, whilst in SIMS it is gained from the detection of molecule ions. Here again the complexity of the formation process often forbids a straightforward interpretation.

For some special cases, chemical bonding can be revealed by AES. It is seen in the fine structure of Auger spectra. Figure 4 demonstrates such a case for

Table 1. Characteristic features of the four most important surface-analysis techniques

	ESCA	AES	SIMS	ISS
Principle				
Excitation	photons	electrons	ions	ions
Emission	electrons (E)	electrons (E)	ions (m/e)	ions (E)
Information depth (monolayers)	3-10	2-10	1-3	1
Detection limit				
ppm	1000	1000	1	1000
g/cm^2	10^{-10}	10^{-10}	10^{-13}	10^{-10}
Difference in elemental sensitivities (factor)	10	10	10^5	10^2
Detection capability				
Elements	$z > 1$	$z > 2$	all	$z > 1$
Isotopes	no	no	yes	restricted
Chemical bond	yes	special cases	indirect	no
Depth profiles	+sputtering	+sputtering	yes (inherent)	yes (inherent)
Advantage	direct inform. on chemical bond, minimum influence on surface comp. (important, *e.g.*, for organic compounds)	almost matrix-independent elemental sensitivity ratios, relatively easy to calibrate, high lateral resolution ($< 1\ \mu m$)	detection of all elements (+isotopes) good detection sensitivity (≤ 1 ppm), high lateral resolution ($\leq 1\ \mu m$)	analysis of outermost atomic layer, information on its structure
Restrictions	detection limit ≤ 0.1 at%, no H detection, limited lateral resolution (≥ 1 mm)	detection limit ≤ 0.1 at% no H and He detection	large elemental sensitivity differences, strong matrix effects, difficult to calibrate	insensitive for light elements, low mass resolution for heavy elements

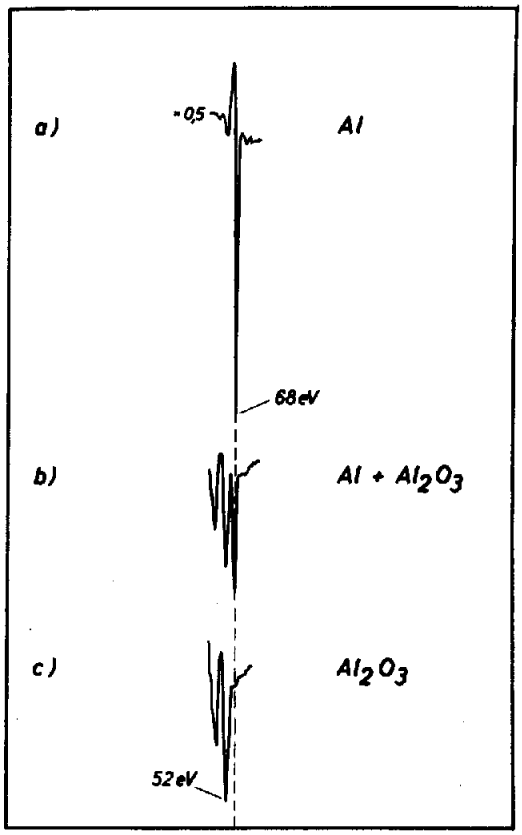


Fig. 4. LVV Auger peaks of Al from (*a*) metallic Al; (*b*) both metal and oxide; (*c*) oxide only. From Ref. 29 (by permission of Springer-Verlag).

the Al LVV Auger transition in elemental aluminium and in the oxide. In AES, quantitative surface analysis is limited by the inelastic mean free path or escape depth of Auger electrons giving a specific attenuation length. Figure 5 shows the relation of this quantity to electron energy for a variety of materials. The typical range for ESCA or AES energies is from about 0.4 to 3 nm in metals.[13] It is slightly higher in oxides and may be as high as 10 nm in organic materials.[13]

The attenuation length or escape depth is defined as the distance over which the number of Auger or photo electrons decreases to $1/e$ of its original value, a reasonable definition if a Lambert–Beer exponential decay law is followed. It means that there is also information from much deeper layers. For example, a 1% elemental concentration in the first layer will show the same signal intensity as a 100% concentration at a depth of about five times the escape depth, or about 5 nm for metals in the mean energy range. This sometimes causes more or less ineffective discussions about what depth we can "see" with AES or ESCA, because in ESCA the signal-to-noise ratio is often improved by using extended measurement times.

An illustration of the problem of sampling depth is given in Fig. 6 for the comparison of homogeneous depth distribution with that for a component A is essentially concentrated at the surface. For a certain escape depth λ, we may get the same signal intensity, so we cannot differentiate between the two cases without additional information. This effect may cause appreciable difficulties in quantification of AES.

Fortunately, there are two possibilities for at least deciding whether an element is concentrated in the first few layers or deeper in the bulk. The first is based on the energy-dependence of the electron escape depth. Auger spectra of the heavier elements show peaks at low and high energies with correspondingly low and high escape depths. Figure 7 shows an example for fractions of a monolayer of tin on a (111) copper surface[16] obtained during surface segregation experiments.[17] If the tin concentration as seen from the Auger peak-to-peak heights of the Sn signal is increased, a corresponding decrease of the 60- and

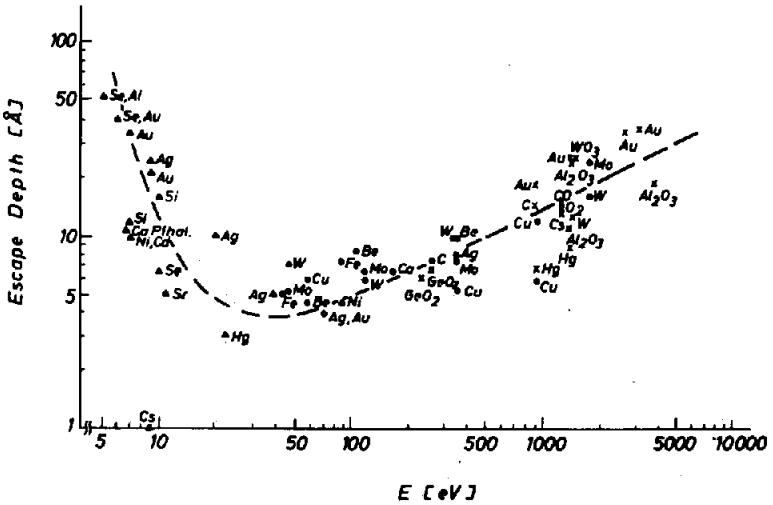


Fig. 5. Mean escape depth (attenuation length) of mono-energetic electrons in AES and ESCA, after Ref. 43 (by permission of North-Holland Publishing Co. Ltd.).

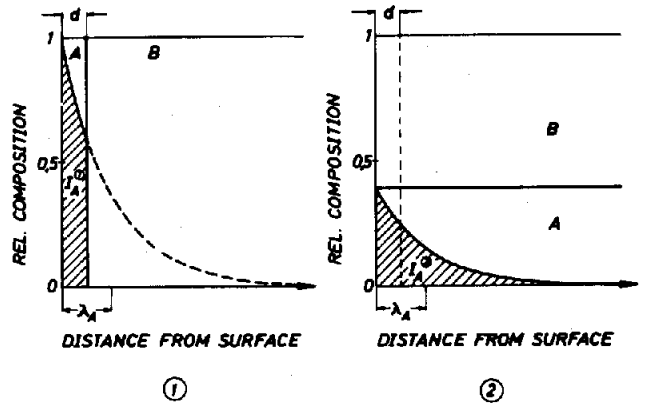


Fig. 6. Escape depth and quantification in electron spectroscopy (AES, ESCA): $I_A^{(1)} = I_A^{(2)}$ in spite of different composition of surface layer d in (1) and (2).

920-eV Auger peaks of the copper matrix is observed. We recognize that the decrease of the low-energy signal (with lower escape depth) is much more pronounced. This indicates enrichment of tin in the outermost layer. If the tin concentration were homogeneously distributed, both signals would decrease with the same gradient.

The second possibility is an artificial reduction of the information depth (defined perpendicular to the surface) by variation of the emission angle.[18] In this case, the effective attenuation length is reduced by a factor equal to the cosine of the angle.

A limiting experimental condition of any reliable surface analysis is that no compositional change should occur during the gathering of information. That means, for example, that the partial pressure of reactive gases should be kept very low, preferable in the ultrahigh vacuum region of 10^{-10} mmHg. Higher partial pressures may lead to a build-up of contamination layers during analysis.[19]

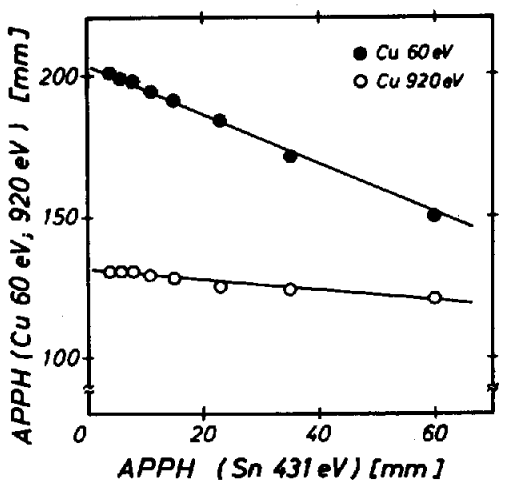


Fig. 7. Decrease of Cu (60 eV) and Cu (960 eV) Auger-signal intensity during the build-up of a tin segregation layer (monitored by the Sn 431-eV Auger signal) on a Cu (111) surface. After Ref. 29 (by permission of Springer-Verlag).

Another very restrictive condition is the requirement that there should be no beam-induced alteration in the sample surface,[20–22] which may occur by diffusion and segregation of elements from the bulk, induced by heat dissipation[21] or by desorption of surface constituents induced by the primary beam.[22] These effects are less pronounced in ESCA and are expected to be most detrimental in the modern Auger microprobes, where high electron current-densities are applied.[23]

We have seen that any of the techniques outlined has its advantages and shortcomings with respect to a particular demand. Therefore we cannot unequivocally decide which of them is best suited for general surface analysis. The answer to such a question depends entirely on the problem to be solved and often only a combination of several methods proves successful.

THIN FILM ANALYSIS

Basic concepts

Let us now consider thin-film analysis in a more specific sense. Figure 8 shows the principles. We have already seen that by a proper use of the variable escape depth of the photo or Auger electrons in AES and ESCA some information can be obtained on elemental or compound distribution in thin films to a depth of about 5 nm. For deeper penetration, there exists at present only one non-destructive method, namely Rutherford back-scattering of high-energy ions in the MeV region (RBS).[24,25] This method has unique quantitative capabilities with respect to scale of concentration and depth. However, because of its poor mass separation and depth resolution and the experimental problem of availability of particle accelerators, it is felt to play a minor role at present.

The remaining methods of thin-film analysis are destructive techniques,[26] that is, in principle they require sectioning of the sample and subsequent analysis. Mechanical sectioning is rather limited with respect to depth resolution, giving rather "thick"

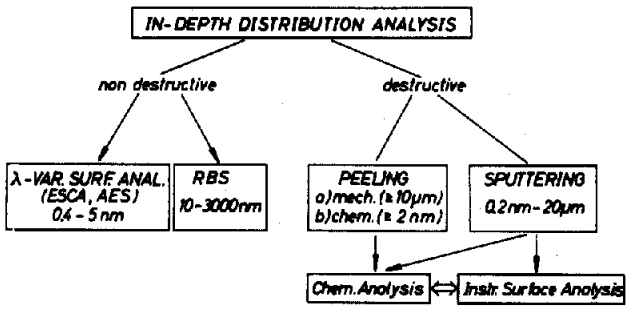


Fig. 8. Principles of Thin-Film Depth-Profiling Analysis[41] (by permission of Elsevier Publishing Co. Ltd.).

ɔles (about 1 μm). Chemical "peeling" techniques yield depth resolution (or depth region separ-ıs) of about 5 nm but are limited to particular ɪrials.[27]

ıother kind of "peeling" technique, which is by he most extensively used for thin-film analysis, ısed on sputtering.[3,10,26,28] Because sputtering ates on the atomic scale, in principle a depth ution in this range should be obtainable. It is y seen that surface analysis in conjunction with ɛring methods is the most direct way of obtain-n-depth concentration profiles. However, sputter-followed by chemical analysis of the sputtered rial is an alternative method which sometimes ıises more reliably quantitative results.[28] A cross-ɛ by both methods is therefore highly desirable.

sputtering, we mean surface erosion by the fol-ıg process. The impingement of primary particles nally noble-gas ions of sufficiently high energy— hundreds to some thousands of eV) causes par- of the solid to leave the surface: they are sput- away. Layers beneath the topmost layer are sub-ɛntly laid free and can be studied by a surface-ʏsis method.

ıe most direct method of thin-film analysis is untered in SIMS, where the sputtered species selves are analysed. We can easily see that in ɨiple there are two ways of using thin-film analysis methods in combination with sputtering,[32] as indicated in Fig. 9. We can analyse the surface remaining after a certain sputtering time, or the sputtered species itself. Both methods should give the same results, if the sputtering process operates by homogeneous layer by layer erosion. Unfortunately, this is generally not the case. With respect to the sputtering, both methods are complementary, so combined use of a method of each type will reveal information on details of the sputtering process.

Capabilities and limitations

Let us have a brief look at the principles of data evaluation shown in Fig. 10.[29] We will get the desired concentration distribution with depth z from the measured raw data profile, which consists of an intensity signal (*e.g.*, electron current in AES and ESCA or secondary-ion current in SIMS and ISS) *vs.* a certain sputtering time. To a first approximation, the concentration is evaluated by quantitative surface analysis, and the depth evaluation is done by a determination of the sputter removal rate dz/dt. If dz/dt is not constant, as for high concentration-alterations of species with different sputtering yields, a depth calibration is rather difficult. The influence of information depth on depth distribution evaluation seems to be manageable, but the most severe problem comes

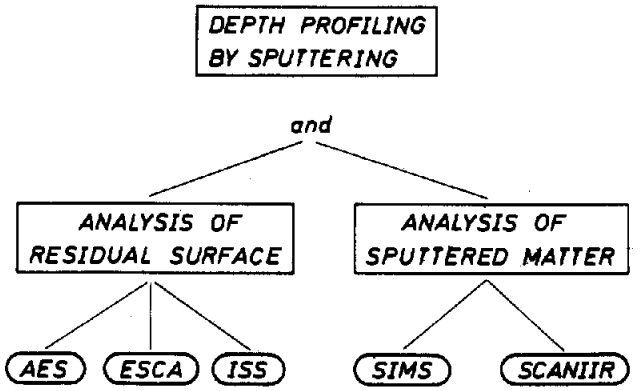


Fig. 9. The complementary methods of thin-film analysis by sputtering (modified after Ref. 32). For abbreviations see Fig. 2.

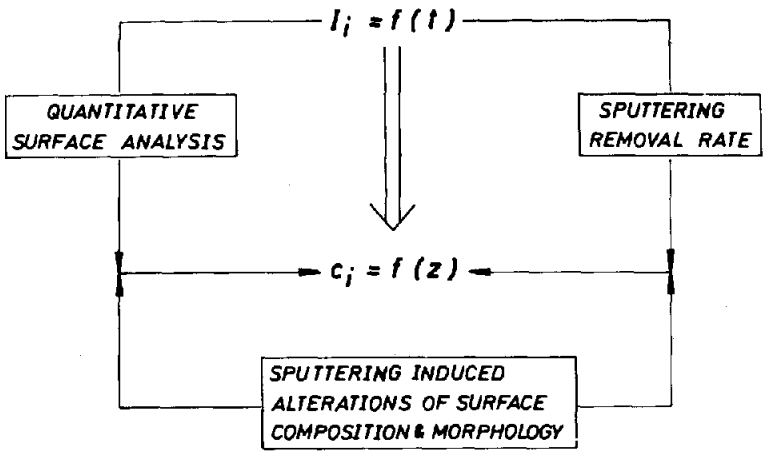


Fig. 10. Composition–depth profile evaluation, $c_i = f(z)$, from measured data, $I_i = f(t)$.

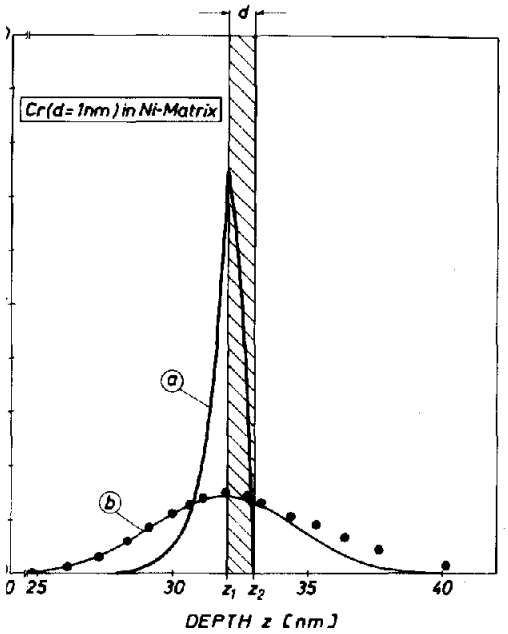
from the alteration of the surface layer by the sputtering process itself.[26] In contrast to the oversimplified picture outlined above, a more realistic view of sputtering has to account for effects of the following types.[3,26,31,32]

Structural and chemical damage of the sample may occur, up to the mean range of the primary projectiles.[33] Primary ions and surface atoms of the specimen are implanted into deeper layers. Owing to severe damage of the first few layers, enhanced diffusion may occur. Furthermore, selective sputtering of different species causes enrichment of the lower sputtering-yield components in the surface layer.[34] Besides these effects, surface roughness,[35] the influence of defect and crystal structure on sputtering yields together with instrumental effects such as non-uniform primary-ion distribution or analysis signals from crater walls must be taken into account.[26,31,36] The gloominess of this picture is somewhat lightened by the depth profiles found in the literature, which seem not too bad with respect to what was expected.

The main reason, in the author's opinion, is that by careful experimental set-up and not too unfavourable conditions of sample composition, quite a number of the effects mentioned may be kept reasonably small, some may tend to cancel and some may even prove beneficial with respect to the accuracy of a depth-profile evaluation. A measure of this accuracy can be given in terms of depth resolution, which is generally defined as the response function of the measured signal if sputtering through an atomically-smooth step-function concentration profile is performed. The shape of a Gaussian integral function is very often found experimentally.[26,29,36–38] The occurrence of this shape can be explained if we regard the sputtering process as purely statistical in nature and operating only at the sequentially liberated first surface layers. This leads to a micro-roughening of the surface, described by a Poisson distribution for the fraction of each layer contributing to the total surface after a certain sputtering time.[26,29] With this assumption, depth profiles can be calculated if rectangular "real profiles" are originally present.[39] For a film thickness of more than about ten atomic layers the Poisson distribution is approximately equal to a Gaussian distribution and the depth resolution is given by twice the standard deviation σ, which is proportional to the square root of the depth.[26,29,30]

If all dynamic effects occurring during sputtering, such as knock-on and ion mixing or preferential sputtering, diffusional as well as instrumental effects can be neglected, and the square-root relation should apply.[31] In most metallic systems this seems to be the case, as shown by a comparison between measured values and theoretical prediction for a variety of metallic systems. This simple model can be extended to cover also effects of escape depth (ESCA, AES), instrumental effects and so on.[31]

The effect of the escape depth λ in AES can be estimated since the λ values are rather well known.[13] The Auger intensity varies by an exponential decay function $\exp(-z/\lambda)$ where z is distance of the respective layer from the surface.[13,29] If the sputtering proceeded like ideal micro-sectioning, we would then expect an intensity profile as depicted in Fig. 11 for the case of sputtering through a thin sandwich layer of an element A in a matrix B. The λ-effect generally shifts the intensity profile to a smaller apparent depth and flattens the slope of the original profile. The points in Fig. 11 show the AES result obtained by sputtering through a 1-nm thick chromium layer in a nickel matrix (at a depth of 32 nm) with 1-keV Ar^+ bombardment.[39] The observed broadening due to sputter micro-roughening is much larger than that expected from the λ-effect alone. However, the λ-effect can be corrected, which is at least a first step in profile deconvolution.[30,40,41] An example is given in Fig. 12. Here, an AES sputter profile of an electrochemically produced niobium oxide layer on niobium with known thickness (80 nm) is shown. After correction for the λ-influence (taking the most appropriate λ values for oxygen in Nb_2O_5 and for Nb in the metal) the interfaces of the Nb peak and the O peak are



11. Depth profiling through a $d = 1$ nm thick Cr rich layer in Ni at depth $z_1 = 32$ nm beneath the al surface[30,39] (by permission of Springer-Verlag). cpected measured profile for ideal micro-sectioning lo escape-depth correction alone ($\lambda_{Cr} = 0.7$ nm); lculated profile for a depth resolution $\Delta z = 5.4$ nm.[39] ● Measured data, Cr (529 eV) Auger signal.[39]

r together (ideally they should be at the same ı and the profile broadening is more similar. ere still remain all the other compositional alter- s induced by the primary excitation, as discussed e, which distort the surface and tend to broaden rofile.[30]

CONCLUSIONS

Future development of surface analysis will comprise more sophisticated data acquisition and above all a combined application of several techniques to cancel some of their individual shortcomings.

The most important and challenging problems in elemental thin film and surface analysis are as follows:

(1) The problems of "samples from the real world", *i.e.* that all the techniques work only under high-vacuum conditions ($p < 10^{-4}$ mmHg) and therefore a surface cannot be studied under normal ambient conditions. This fact will restrict surface analysis to performance of simulation experiments and provide indirect proofs in many cases.

(2) The problem of quantification of surface analysis is two-fold. First, use of standards is much more difficult than in bulk analysis because no multi-component surface layer that is really reproducible and stable on an atomic scale is available. Therefore we are restricted to pure element standards. Secondly, quantification without standards is possible if the decisive physical parameters underlying the analytical process are known. These comprise, *e.g.*, cross-sections for excitation and emission (ESCA, AES), back-scattering (AES) and escape depth (ESCA, AES), ion-neutralization probabilities (ISS), sputtering yields and ionic-emission probabilities (SIMS). Knowledge of these parameters is increasing thanks to the progress of fundamental research.

(3) Alterations of the surface by the influence of X-rays or electron and ion beams is a most important restriction in surface analysis. Furthermore, in thin-film depth-profile analysis by sputtering, the artifacts induced by the ion beam have to be carefully con-

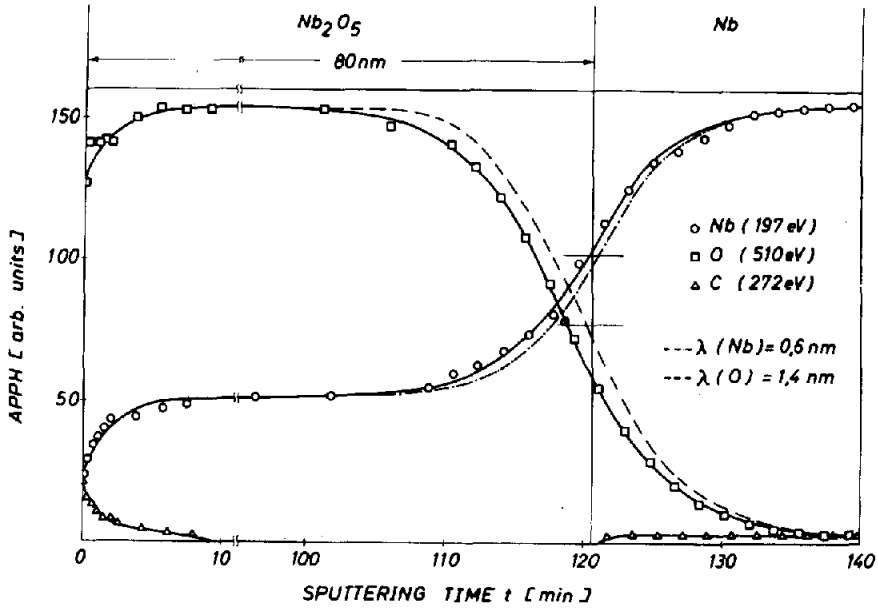


Fig. 12. AES sputtering profile of an 80-nm thick Nb_2O_5 layer on Nb.[30] Dashed lines represent the O and Nb profiles after λ correction, with λ_{Nb} (197 eV) = 0.6 nm, λ_O (510 eV) = 1.4 nm. (By permission of Springer-Verlag.)

trolled. Again the steady accumulation of experience will at least show what can be expected and how these various influences may be kept small. A better understanding of the processes of the interaction of different kind of primary beams with the surface is the key to further improvement in obtaining reliable data from surface and thin-film analysis.

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MIKROANALYTISCHE UNTERSUCHUNGEN ZUR LÖSLICHKEIT VON NATURSTOFFEN IN ÜBERKRITISCHEM KOHLENDIOXID

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Zusammenfassung—Mit Hilfe einer Mikroextraktions-Apparatur wird das druckabhängige Löslichkeitsverhalten einiger Naturstoffe in komprimiertem Kohlendioxid von 80 bis 2000 bar untersucht. Die Löslichkeitswerte für verschiedene Verbindungen sind stark unterschiedlich, steigen aber unter Druck. Es besteht ein linearer Zusammenhang zwischen dem Logarithmus der Löslichkeit und dem der Dichte des komprimierten Gases. Die Temperatur beeinflußt ebenfalls neben dem Druck die Lösungseigenschaften des Kohlendioxids.

Die Kenntnis der Eigenschaften komprimierter Gase ist Voraussetzung für ihre Anwendung als Lösungs- und somit auch als Extraktionsmittel. Besonders wichtig sind neben den grundlegenden physikalisch-chemischen Daten die Löslichkeitsuntersuchungen bei verschiedenen Drücken und Temperaturen mit Substanzen unterschiedlicher Konstitution. Als Gas diente Kohlendioxid, da es zu den am besten beschriebenen Gasen zählt und auch bereits als Extraktionsmittel häufig Anwendung fand.[1]

Mit verschiedenen Naturstoffen wurden von uns bereits früher im Druckbereich zwischen 70 und 400 bar bei 40° Extraktionsversuche mit fluiden Gasen in direkter Kopplung mit der Dünnschicht-Chromatographie durchgeführt.[2–4] Dabei konnten Faustregeln über die Extrahierbarkeit der Substanzen mit überkritischem Kohlendioxid und mit Distickstoffoxid in diesem Bereich aufgestellt werden. Es ergaben sich gute Zusammenhänge zwischen der Konstitution der Substanz und ihrer Löslichkeit als Funktion des Druckes.

Erste quantitative Löslichkeitsbestimmungen polarer Naturstoffe, wie z.B. von Aminosäuren und Zuckern, in überkritischen Gasen bei Drücken zwischen 300 and 2500 bar ergaben bei unterschiedlichen Löslichkeiten der einzelnen Substanzen nur eine geringe Abhängigkeit der Löslichkeit vom Druck.[5] Die Substanzkonzentrationen im überkritischen Gas sind auch bei Drücken von 2500 bar so gering, daß eine Anwendung der bisher untersuchten Gase für die Extraktion polarer Naturstoffe nicht in Betracht kommt. Für diese Substanzgruppe könnten deshalb andere Gase, wie z.B. Ammoniak, von Interesse sein.

Vor allem für lipophile Naturstoffe sollte überkritisches Kohlendioxid deshalb ein geeignetes Extraktionsmittel sein. Quantitative Löslichkeitsuntersuchungen stellen eine Voraussetzung für die praktische Anwendung dieses Gases dar.

EXPERIMENTELLER TEIL

Für die nachfolgenden Untersuchungen wurden einfache Naturstoffe unterschiedlicher Flüchtigkeit ausgewählt, die bereits in früheren Arbeiten[3] als Modellsubstanzen dienten. Wichtig war die sichere Erfassung auch geringer Substanzmengen mit spektralphotometrischen Methoden. Die früheren Untersuchungen sind als Vorversuche zu werten, aus denen die Größenordnung der zu erwartenden Löslichkeiten ersichtlich wurde.

Apparatur zur Löslichkeitsbestimmung

Den Aufbau der Apparatur zur Löslichkeitsbestimmung im Mikromaßstab zeigt schematisch Abb. 1. Kompressorteil und Extraktionseinrichtung befinden sich in einem thermostatisierten und geräuschdämpfenden Gehäuse. Das Prinzip des Druckerzeugungssystems wurde bereits ausführlich beschrieben.[2]

Der Mikroautoklav (n) nimmt die Probesubstanzen auf. Druck und Temperatur des komprimierten Gases werden direkt am Autoklaven durch entsprechende Meßeinrichtungen (m, o) gemessen und können mit dem Mehrkanalschreiber (s) registriert werden. Das verdichtete Kohlendioxid entspannt sich am Ende der an das Ausgangsventil (d_4) angesetzten auswechselbaren Spezialkapillare auf Atmosphärendruck. Die im Gas gelöste Substanz fällt nach der Entspannung aus und wird in einem Glastrichter (p) gesammelt. Die reproduzierbare Regelung der Strömungsgeschwindigkeit erfolgt mit fest eingestellten Strömungswiderständen. Dazu dienen auswechselbare Edelstahlkapillaren von 15 bis 20 mm Länge, deren Öffnungen von 100 μm mit Edelstahldrähten verschiedener Dicken im gewünschten Maß verengt werden. Die Kapillaren sind in 1/16-in. Hochdruckrohr eingelötet und am Ausgangsventil druckfest verschraubt. Die Durchflußraten können auf diese Weise ab etwa 0,2 Nl*/min eingestellt werden.

Ein nachgeschalteter Massendurchflußmesser (q) mit angeschlossenem elektronischem Integrator bestimmt die abströmende Gasmenge.

Durchführung der Bestimmungen

Die zu extrahierenden Substanzen werden in Lösung auf etwa 100 mg gereinigte Quarzwolle gleichmäßig verteilt. Nach vollständigem Abdampfen des Lösungsmittels wird

* 1 Nl = 1 Liter bei 0°C and 1 bar.

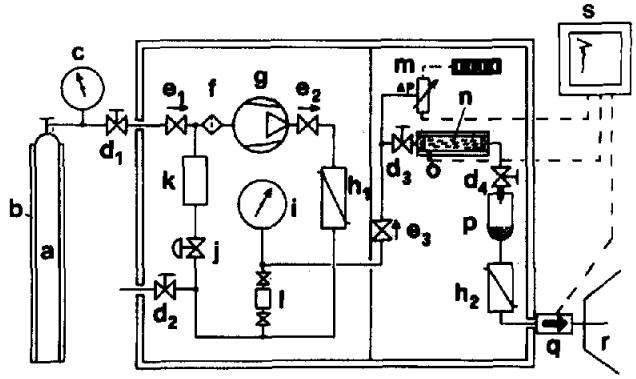

Abb. 1. Hochdruckextraktionsanlage zur Löslichkeitsbestimmung im Mikromaßstab: a, Druckflasche; b, regelbarer Heizmantel; c, Vordruckmanometer; d_1, bis d_3, Hochdruckventile; d_4, Hochdruckventil mit Spezialkapillare; e_1, bis e_3, Rückschlagventile; f_3, Hochdruckfilter; g, Membrankompressor; h_1, h_2, Wärmeaustauscher; i, Hochdruckmanometer; j, Druckhalteventil; k, Puffervolumen; l, Dämpfungsvorrichtung; m, DMS-Druckaufnehmer mit Anzeigeeinheit; n, Mikroautoklav; o, Thermoelement; p, Abscheider; q, Strömungsmesser; r, Absaugvorrichtung; s, Schreiber.

die mit 10 bis 100 mg Substanz beladene Quarzwolle in den Proberaum des Autoklaven gegeben.

Die Extraktionen erfolgen vorzugsweise bei 40° und bei Drücken zwischen 80 and 200 bar, in Einzelfällen zusätzlich bis 2000 bar. Für jede Druckstufe werden mindestens 3 Versuche durchgeführt.

Durch Öffnen von Ventil (d_3) füllt sich der Proberaum bis zum eingestellten Gasdruck mit Kohlendioxid. Nach einigen Minuten wird das Ausgangsventil (d_4) geöffnet und das komprimierte Gas entspannt sich am Ende der Kapillare. Die gelöste Substanz fällt aus und wird im Filter des Glastrichterabscheiders (p) aufgefangen.

Die quantitativ ausgefallenen Substanzen werden anschließend mit 10,0 ml eines geeigneten Lösungsmittels portionsweise eluiert. Die mit Quarzwolleteilchen des Filters verunreinigten Lösungen werden über Membranfilter geringer Porenweite (0,15 μm) filtriert.

Alle untersuchten Naturstoffe werden direkt photometrisch in Lösung bestimmt. Die Auswertung erfolgt nach Aufstellung von Eichkurven, wobei die Meßwellenlängen der einzelnen Substanzen durch vorherige Spektranaufnahme mit einem registrierenden Spektralphotometer bestimmt werden. Je nach Substanzkonzentration können entweder Quarzküvetten mit 1,00 cm Schichtdicke, oder es müssen Quarzmikroküvetten mit 5,00 cm Schichtdicke benutzt werden.

ERGEBNISSE UND DISKUSSION

Es wurden 5 aromatische Carbonsäuren und ein entsprechender Ester untersucht. Vier Carbonsäuren bilden eine homologe Reihe mit Hydroxylgruppen unterschiedlicher Anzahl und Anordnung. Abbildung 2 zeigt die Druckabhängigkeit der Löslichkeit der Verbindungen in überkritischem Kohlendioxid bei 40°.

Die Benzoesäure, in der Reihe zunehmender Polarität die lipophilste Carbonsäure, läßt sich qualitativ bereits unterhalb von 70 bar nachweisen. Die Benzoesäurekonzentration im Gas beträgt bei 80 bar 200 μg/Nl*, d.h. mehr als 100 ppm (μg/g).

* 1 Nl Kohlendioxid entspricht 1,78 g.

Ab 85 bar steigt die Löslichkeit sehr stark an, bei 100 bar können bereits 3,5 mg und bei 150 bar mehr als 8,5 mg Nl Gas extrahiert werden.

Die auf Grund der Hydroxylgruppe in *ortho*-Stellung etwas polarere Salicylsäure ist schwerer löslich: ihre Konzentration im überkritischen Gas beträgt bei 150 bar nur etwa 2 mg/Nl. Der Unterschied zwischen der Salicylsäure und der *trans*-Zimtsäure dagegen ist geringer. Von dieser Arylalkencarbonsäure lösen sich bei 150 bar etwas über 1 mg/Nl.

Eine wesentlich geringere Löslichkeit zeigt die mit zwei Hydroxylgruppen in 2,5-Stellung versehene Gentisinsäure: nur etwa 15 μg/Nl können bei 150 bar mit überkritischem Kohlendioxid extrahiert werden, was eine mehr als 100 fach niedrigere Löslichkeit gegenüber der Salicylsäure bedeutet.

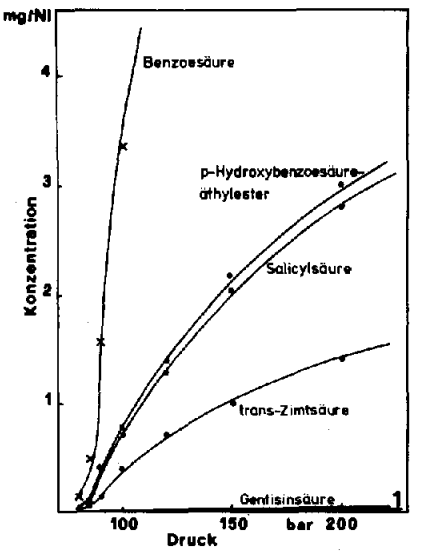

Abb. 2. Druckabhängige Konzentration verschiedener Feststoffe in überkritischem Kohlendioxid bei 40°. 1 *p*-Hydroxybenzoesäure, Bezeichnung der weiteren Kurven in der Abb.

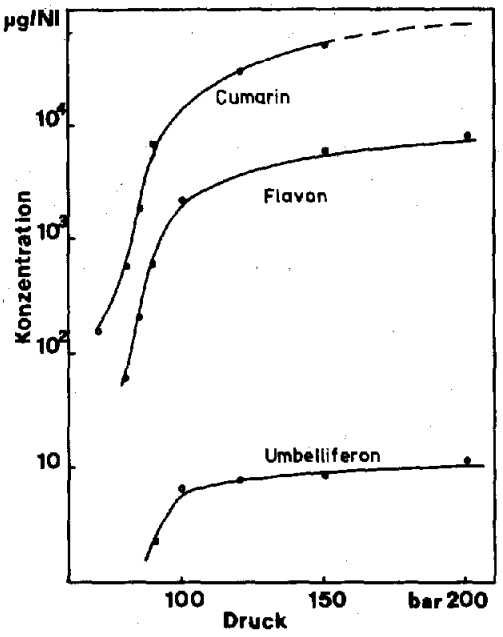

Abb. 3. Druckabhängige Konzentration von Pyronderivaten in überkritischem Kohlendioxid bei 40°.

Steht eine Hydroxylgruppe in *para*-Stellung zur Carboxylgruppe, dann resultiert eine überraschend starke Verringerung der Löslichkeit. Für *p*-Hydroxybenzoesäure beträgt die Substanzkonzentration im Gas bei 150 bar nur 10 µg/Nl. Wird die Carboxylgruppe verestert, steigt die Löslichkeit wieder stark an, wie in Abb. 2 am Beispiel des *p*-Hydroxybenzoesäureäthylesters zu erkennen ist.

Die Druckabhängigkeit der Löslichkeit verschiedener Pyronderivate bei 40° zeigt Abb. 3. Das Cumarin, ein α-Pyronderivat, löst sich vergleichsweise gut. Die Cumarinkonzentration beträgt im überkritischen Kohlendioxid bereits bei 83 bar 1 mg/Nl. Die Löslichkeit nimmt mit steigendem Druck so stark zu, daß bei 150 bar eine Konzentration von 50 mg/Nl erreicht wird.

Die Einführung einer zusätzlichen Phenylgruppe bedingt ein höheres Molekulargewicht, die Löslichkeit verringert sich. Bei 150 bar können etwa 5,5 mg Flavon pro Nl Kohlendioxid extrahiert werden.

Das mit einer Hydroxylgruppe versehene Cumarinderivat Umbelliferon zeigt bei vergleichbarem Molekulargewicht gegenüber dem Cumarin eine Löslichkeit von nur 6 µg/Nl unter den gleichen experimentellen Bedingungen. Das Cumarin selbst läßt sich also fast um den Faktor 10^4 besser extrahieren als sein in 7-Stellung hydroxyliertes Derivat. Eine Extraktion höher hydroxylierter Cumarinderivate war nicht nachweisbar.

Einige hydrophile Substanzen wurden bis 2000 bar untersucht. Ihre druckabbängigen Löslichkeitskurven sind in Abb. 4 zu sehen. Die relativ höchsten Konzentrationswerte in überkritischem Kohlendioxid zeigt die Gentisinsäure. Mit 50 µg/Nl bei 2000 bar übertrifft sie die *p*-Hydroxybenzoesäure um 10 µg/Nl, während sich das Umbelliferon bei 2000 bar zu 30 µg/Nl löst.

Vergleicht man diese Werte mit den bei 80 bar gefundenen Substanzkonzentrationen, läßt sich eine etwa 100 fache Konzentrationserhöhung zwischen 80 und 2000 bar feststellen. Die größte Steigerung erfolgt dabei unterhalb von 200 bar. Zwischen 500 and 2000 bar steigt die Löslichkeit lediglich um den Faktor 2 an. Die Formen der einzelnen Löslichkeitskurven zeigen vergleichbare Merkmale, die mit den übrigen untersuchten Substanzen übereinstimmen.

Bis 85 bar nimmt die Löslichkeit in überkritischem Kohlendioxid bei 40° nur wenig zu. Zwischen 85 und etwa 100 bar steigt die Substanzkonzentration im Gas stark an, die Wendepunkte der Löslichkeitskurven liegen bei 90 bis 100 bar, danach flachen sie ab. Je

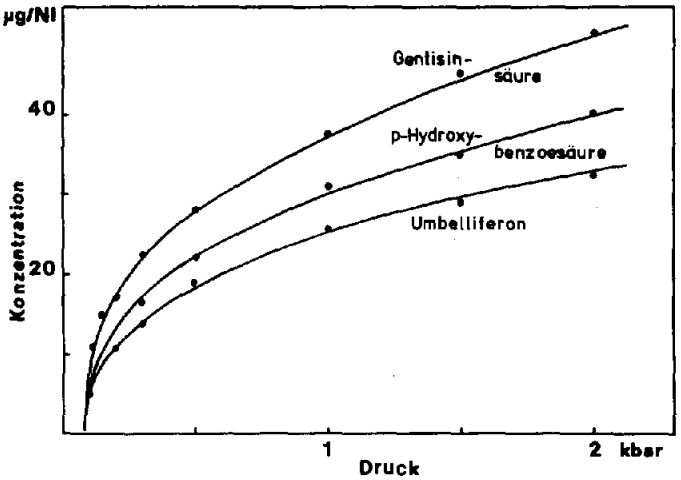

Abb. 4. Druckabhängige Konzentration hydrophiler Naturstoffe in überkritischem Kohlendioxid bei 40°C.

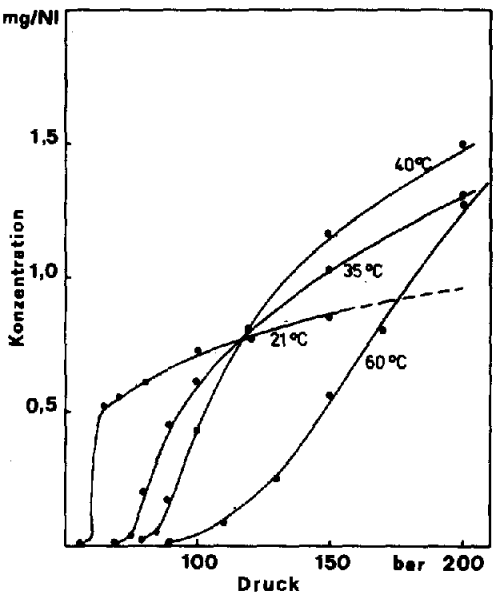

Abb. 5. Druckabhängige Konzentration von Coffein in komprimiertem Kohlendioxid bei verschiedenen Temperaturen.

höher die Polarität der Substanzen ist, umso flacher verlaufen im allgemeinen die Kurven.

Die druckabhängigen Lösungseigenschaften des komprimierten Kohlendioxids wurden bei 4 verschiedenen Temperaturen bestimmt. Als Modellsubstanz diente Coffein. Die Löslichkeitsisothermen (Abb. 5) bei 21, 35 und 40° zeigen die bekannte *s*-förmige Gestalt. Bei 21° steigt die Löslichkeit sprunghaft mit der Verflüssigung des Gases an, um mit weiter steigendem Druck nur noch langsam zuzunehmen. Oberhalb der kritischen Temperatur (35°) ist der Anfangsteil der Isotherme gegenüber der 21°-Isotherme zu höheren Drücken verschoben. Der Schnittpunkt dieser Kurven liegt bei etwa 110 bar.

Eine um 20° höhere Temperatur (60°-Isotherme) verschiebt den unteren Teil der Löslichkeitskurve nochmals zu höheren Drücken. Die Steigung ist in diesem Teil relativ gering, ab etwa 130 bar übertrifft sie jedoch die Steigung der übrigen Isothermen, so daß diese bei Drücken über 200 bar geschnitten werden.

Eine Erhöhung der Temperatur des komprimierten Kohlendioxids hat bei gleichbleibendem Druck zunächst eine Erniedrigung der Konzentration des gelösten Stoffes im Gas zur Folge. Bei Erhöhung des Druckes steigt dann die Löslichkeit stärker an und übertrifft schließlich die gelöste Stoffmenge bei niedrigerer Temperatur. Für die Bestimmung der Konzentration von Substanzen im verdichteten Gas sind der Druck und die Temperatur gleichwertige Parameter.

Der Partialdruck der untersuchten Naturstoffe im komprimierten Gas ist bei unbeeinflußter Verdampfung, also bei Anwendung der idealen Gasgesetze unter den experimentellen Bedingungen sehr gering, deutlich unter 1 mbar. Mit zunehmendem Gasdruck nimmt der Partialdruck weiter ab.

Dagegen ist die gemessene Substanzkonzentration sehr hoch. Diese Tatsache macht deutlich, daß das verdichtete Gas Wechselwirkungen mit den Substanzteilchen eingeht; es ist in der Lage, die Probesubstanzen in der Gasphase zu lösen.

Ein Vergleich zwischen den unter der Annahme idealer Bedingungen berechneten und den tatsächlich gemessenen Substanzkonzentrationen im überkritischen Kohlendioxid bei 40° und 100 bar ist in Tab. 1 zusammengestellt. Bereits bei einem Druck von 100 bar läßt sich eine 10^4- bis 10^5-fache Erhöhung gegenüber den berechneten Werten feststellen. Mit zunehmendem Druck steigt dieses Verhältnis noch an, wie aus den einzelnen druckabhängigen Löslichkeitskurven zu sehen ist.

Bereits Diepen und Scheffer[6] konnten diese enormen Unterschiede zwischen berechneten und gemessenen Substanzkonzentrationen im Gas bei ihren Löslichkeitsbestimmungen von Naphthalin im überkritischen Äthylen feststellen, ebenso den typischen druckabhängigen Verlauf der Löslichkeitskurven.

Trotz der Verschiedenartigkeit der untersuchten Naturstoffe deutet die annähernd gleiche Form der einzelnen Kurven bei 40° darauf hin, daß das Verhalten eines Stoffes im komprimierten Gas hauptsächlich von den druckabhängigen Eigenschaften des Gases selbst bestimmt wird.

Die Löslichkeitskurven ähneln im gesamten Bereich von 80 bis 2000 bar der druckabhängigen Dichteisotherme. Die Zusammenhänge zwischen der Gasdichte und der Substanzlöslichkeit wurden bereits diskutiert.[5] Sie lassen sich bei logarithmischer Auftragung beider Größen als Geraden darstellen, wie in Abb. 6 an einigen Beispielen deutlich gemacht wird. Franck[7] und Rowlinson und Richardson[8] konnten

Tabelle 1. Berechnete und gemessene Substanzkonzentrationen in Kohlendioxid bei 100 bar und 40°

Substanz	F_p,°C	Dampfdruck, *mbar*	Konz. C_0 berechnet, *µg/Nl*	Konz. C_1 gemessen, *µg/Nl*	C_1/C_0
Cumarin	71	$2 \cdot 10^{-2}$	$3{,}2 \cdot 10^{-1}$	14000	$4{,}4 \cdot 10^4$
Benzoesäure	122	$5{,}3 \cdot 10^{-3}$	$7{,}1 \cdot 10^{-2}$	3400	$4{,}8 \cdot 10^4$
Salicylsäure	159	$1{,}2 \cdot 10^{-3}$	$1{,}9 \cdot 10^{-2}$	750	$4{,}1 \cdot 10^4$
trans-Zimtsäure	133	$2{,}9 \cdot 10^{-3}$	$1{,}6 \cdot 10^{-2}$	400	$2{,}5 \cdot 10^4$
p-Hydroxybenzoesäure	214	$2{,}3 \cdot 10^{-6}$	$3{,}6 \cdot 10^{-5}$	6	$1{,}6 \cdot 10^5$

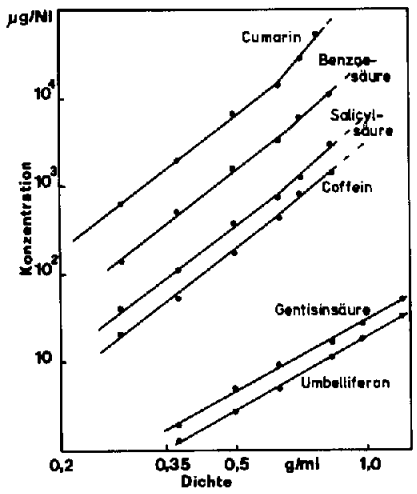

Abb. 6. Dichteabhängigkeit der Löslichkeit von Naturstoffen in überkritischem Kohlendioxid bei 40°.

aufgrund theoretischer Betrachtungen bereits früher vergleichbare Zusammenhänge zeigen.

Durch die Anwendung unserer Mikroextraktionsmethode ist es nun möglich, das Löslichkeitsverhalten der verschiedensten Naturstoffe in überkritischem Kohlendioxid, darüberhinaus aber auch in anderen interessierenden Gasen, wie z.B. in Distickstoffoxid schnell und einfach zu untersuchen. Wir betrachten diese Messungen als eine wichtige Voraussetzung, um Extraktionsverfahren im technischen Maßstab mit komprimierten Gasen durchführen zu können. Zur Beurteilung des Verfahrens der Extraktion mit komprimierten Gasen müssen im Unterschied zur Flüssigextraktion Löslichkeitsbestimmungen der zu untersuchenden Stoffe herangezogen werden. Die Druck- und Temperatur-abhängigkeit der Löslichkeit muß gemessen werden, um bestmögliche Abtrennung von Begleitstoffen und optimale Ausbeute zu gewährleisten.

Anerkennungen—Der Deutschen Forschungsgemeinschaft danken wir auch hier für die Bereitstellung von Sach- und Personalmitteln im Projekt Sta 56-13.

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Summary—The pressure-dependent solubility of some natural products in gaseous carbon dioxide compressed to pressures in the range 80–2000 bar has been examined with the help of a micro-extraction apparatus. The solubilities vary greatly from one compound to another, but always increase with pressure. There is a linear relationship between the logarithms of the solubility and of the density of the compressed gas. Besides pressure, the temperature also influences the solubility in carbon dioxide.

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WET MINERALIZATION OF ORGANIC MATRICES IN GLASSY CARBON VESSELS IN A PRESSURE-BOMB SYSTEM FOR TRACE ELEMENT ANALYSIS

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Summary—Glassy carbon (Sigradur G®†) is thermally stable up to 600° under atmospheric conditions and has proved to be substantially resistant to many decomposition agents at temperatures up to 250°. It can, therefore, substitute for PTFE vessels in a pressure-bomb device for the wet decomposition of organic and inorganic substances with, *e.g.*, nitric, chloric or hydrofluoric acid or mixtures thereof, in the determination of trace elements. The mineralization can be carried out at temperatures up to 50° higher than with PTFE vessels, which are limited to a maximum of 170°. The higher decomposition temperature, which results in a higher oxidation potential, considerably shortens the decomposition time. On account of the lower content of impurities, particularly of Hg, Ag, Bi, Cd, Se, Te and Sb, the results are more accurate than those obtained with PTFE vessels, if these elements are to be determined in the ng/g range in the resulting solution.

Most of the powerful analytical methods, such as polarography, spectrophotometry, atomic-absorption spectrometry, optical emission spectrometry with HF and UHF plasma excitation (ICP, CMP, MIP), demand dissolved samples for the determination of trace elements in organic and inorganic substances. Therefore a sample decomposition is the first important step of the analytical procedure, which has to meet a series of requirements.[1–3]

(1) The decomposition vessels and apparatus should be made from inert materials with high thermal stability and with low impurity content (to minimize the blanks).

(2) The decomposition of organic samples must be complete to avoid strong interference by organic residues in the determination.

(3) The products must be soluble in small volumes of easily purified acids.[4]

(4) Other sources of systematic error (*e.g.*, adsorption, desorption, volatilization), which increase with decreasing content of the elements to be determined, must be eliminated as far as possible.

(5) The decomposition method should be simple and economical.

For many analytical problems the decomposition of the sample with acids under pressure in sealed PTFE, quartz or noble metal apparatus has proved suitable.[5–9] Various such devices have been reviewed.[10,11] In extreme trace analysis, the above-mentioned rules must especially carefully be taken into account. Because of this we have optimized a PTFE pressure-bomb system,[5] which is commercially available.§ After some years of experience with that system we found the PTFE insert to be unsuitable in some cases,[12] mainly because of its limited thermal and chemical stability, and its relatively high levels of impurities, which cause varying blanks for some elements to be determined in the decomposition solution. In such cases glassy carbon (Sigradur G®†) was found to be more inert and more stable than PTFE at higher temperature, so it is a more suitable vessel material in our pressure-bomb system (Fig. 1). Quartz, which may also be used instead of PTFE, is not resistant to hydrofluoric acid, and has a high risk of breakage.

EXPERIMENTAL

Glassy carbon (Sigradur G®) is produced by carbonizing a three-dimensionally cross-linked synthetic resin.[13,14] It is a hard material without open pores and has a smooth surface impermeable to liquids and gases. The material is isotropic, with breaking strength equal to porcelain, but its thermal shock resistance is much better.

These properties and its high thermal stability in comparison with PTFE (Table 1) are its most important advantages. While PTFE vessels cannot be used at above about 160–200° (depending on their quality), glassy carbon vessels can be used at temperatures up to 250° in presence of nitric, chloric or hydrofluoric acid. There is no penetration of acid or, *e.g.*, mercury vapour through the walls of the decomposition vessel, such as has been found with PTFE by using ^{203}Hg.[12] These diffusion processes cause variable blanks. Adsorption effects are lower than with

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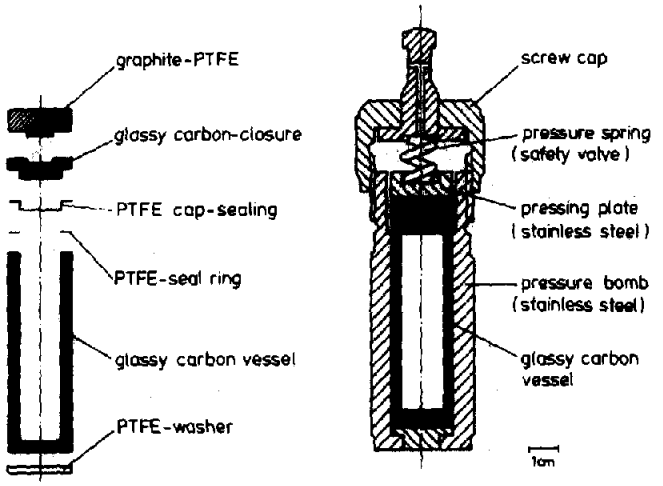

Fig. 1. Pressure decomposition bomb with glassy carbon insert.

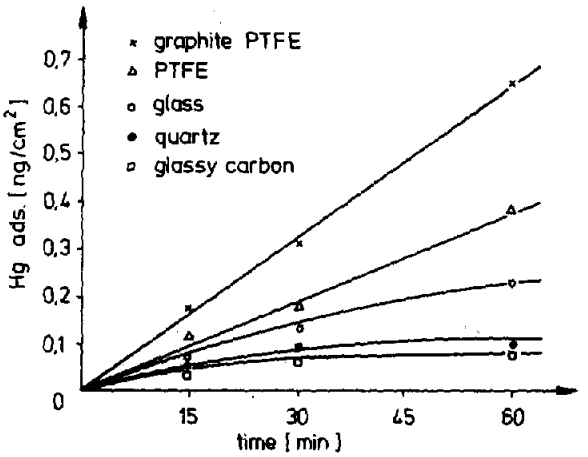

Fig. 2. Adsorption of Hg-vapour on different untreated working materials.

PTFE, as can be shown in the case of mercury (Fig. 2). The risk of breakage under the conditions of a pressure decomposition is low, owing to the similar coefficients of expansion of glassy carbon and the surrounding stainless steel of the bomb.

With respect to purity, Sigradur G® is comparable with other suitable materials, particularly in relation to the toxicologically and environmentally relevant elements such as Hg, Cd, Pb, As, Sb, Se (Table 2). It is also easy to reduce the relatively high content of elements such as Fe, Cu,

Table 1. Comparison of some properties important in a pressure decomposition

Property	Glassy carbon SIGRADUR G®	PTFE	Quartz
Resistance to			
HCl	+(≤200°C)	+(≤160°C)*	+(≤150°C)†
HF	+	+	−
HNO_3	+	+	+
$HClO_3$	+	+	+
$HClO_4$§	+(≤150°C)	+(≤150°C)	+(≤150°C)
H_2SO_4	+	+(≤160°C)	e(≤160°C)
HF/HNO_3 (1:1)	+(≤200°C)	+(≤160°C)	−
alkali	+	+	−
Gas permeability	0	+	0
Adsorption behaviour	see Fig. 2	see Fig. 2	see Fig. 2
Thermal stability	≤220°C	160–200°C*	≤150°C†
Dimensional stability	++	+	++

* Thermal stability depends very strongly on quality.
† Not suitable for decomposition vessels on account of the low coefficient of expansion.
§ Only limited applicability because of danger of bursting.

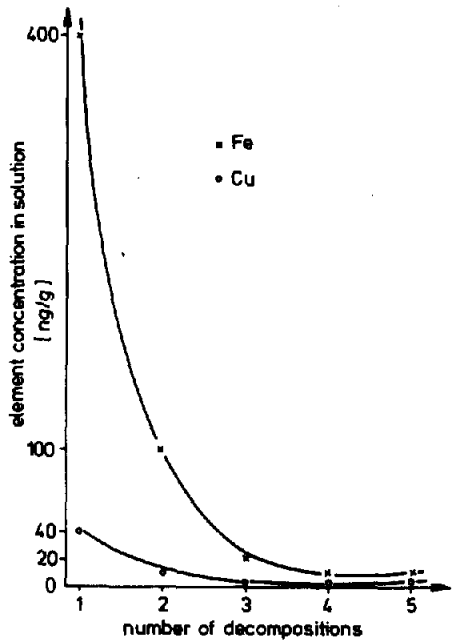

Fig. 3. Reduction of elemental impurities in a glassy carbon vessel by repeated leaching with HNO_3 (70%) under conditions of a pressure decomposition (200°C, 3 hr).

Ti, Sn by leaching with 0.5 ml of nitric acid (70% w/v) under pressure (Fig. 3).

Analyses of the decomposition vessels and of the decomposition solutions by neutron-activation analysis and atomic-absorption spectrometry (Table 3) show that the main part of the impurities is on the surface of the vessel and is not incorporated homogeneously within the whole material. The impurities are transferred during machining. After the leaching treatment, the level of impurities dissolved off the surface does not exceed the normal level found in the acids used. The decisive advantage of glassy carbon over PTFE is, however, its higher thermal stability, which allows an increase of the decomposition temperature up to 220°.

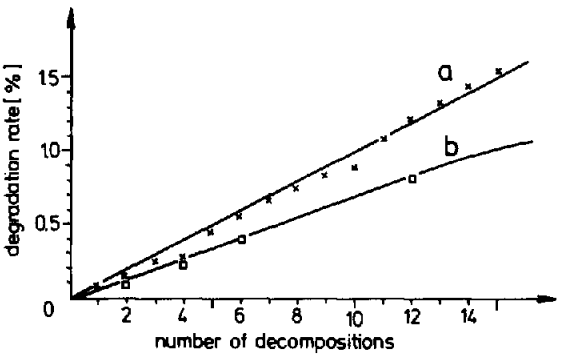

Fig. 4. Loss in weight of glassy carbon after repeated treatment with (*a*) HNO_3 (70%) and (*b*) chloric acid (20% $HClO_3$/7% $HClO_4$) under conditions of pressure decomposition (0.5 ml of acid, 200°C, 3 hr).

Polarographic and spectroscopic investigations prove that mineralization under the conditions of a conventional pressure decomposition with nitric acid at a temperature of 160° is not complete for many organic matrices. The oxidation potential is not sufficient to digest all organic compounds completely (*e.g.*, fats, proteins or heterocyclic compounds may not be decomposed).

The decomposition temperature when glassy carbon vessels are used is limited to about 220°, the softening temperature of the PTFE sealing material which is needed to close the system tightly. Even at this temperature glassy carbon is resistant to nitric acid (70% w/v). The loss of weight of the vessels after 15 pressure decompositions—corresponding to nitric or chloric acid treatment for 45 hr—amounts to about 1.5 and 1%, respectively (Fig. 4). Scanning electron-microscope and light-microscope pictures show that the degradation during acid treatment starts from definite positions, probably corresponding to local impurities at the surface (Fig. 5). The cluster and

Table 2. Impurities ($\mu g/g$) in different materials according to the literature and investigation

Element	SIGRADUR G®	PTFE	Quartz HERALUX®	Quartz SUPRASIL®	Borosilicate glass
B	0.1	—	0.1	0.01	main
Na	0.35	25	1	0.01	main
Mg	0.1	—	0.1	0.1	600
Al	6	—	10–50	0.1	main
Si	80–90	—	main	main	main
Ca	70–90	—	0.8–3	0.1	1000
Ti	12	—	0.8	0.1	3
V	4	—	—	—	2
Cr	0.08	0.03	0.005	0.003	3
Mn	0.1	—	0.01	0.01	6
Fe	2	0.01	0.8	0.2	200
Co	0.002	0.002	0.001	0.001	0.1
Ni	0.5	—	—	—	2
Cu	0.2	0.02	0.07	0.01	1
Zn	0.3	0.01	0.05	0.1	2–4
As	0.05	—	0.08	1×10^{-4}	0.5–22
Cd	0.01	—	0.01	—	1
Sn	25–50	—	—	—	4
Sb	0.01	4×10^{-4}	0.002	0.001	7–9
Hg	*ca.* 0.001	10*	10^{-3}	10^{-3}	—
Pb	0.4	—	—	—	3–50

* Strongly dependent on storage conditions.

Table 3. Reduction of element impurities (*ng/g*) in a glassy carbon vessel by repeated leaching with 0.5 ml of 70% nitirc acid under pressure (160° and 200°C, 3 hr)

Method	Element	Concentration of the element after leaching at 160°C	200°C
Furnace AAS	Fe	≤10	10
	Cu	≤0.5	≤1
	Cd	≤0.5	≤1
	Pb	≤0.5	≤1
	Bi	≤0.5	≤1
INAA	Co	≤0.8	≤1
	Zn	≤1	≤1.5
	Sc	≤0.5	≤0.8
	Ta	≤0.8	≤2.5
	Sb	≤1	≤1
	Cr	≤0.8	≤2

crater formation proceeds during a longer exposure period (Fig. 6), unlike the case with PTFE vessels which are seriously attacked equally over the whole surface (Fig. 7).[15]

Optimization of the decomposition conditions

The oxidation potential of acids *e.g.*, nitric, rises quickly with increasing temperature. It was, therefore, necessary to find the optimal temperature and duration for the decomposition process.

This was done by treating a variety of relevant matrices for various times at various temperatures controlled by means of an electronically regulated heating-block system*, which allows supervision of the decomposition procedure.

During treatment of the sample with nitric acid (70% w/v) organic nitro-compounds will be formed. These, as well as organic macromolecules which are not mineralized completely at temperatures ≤160°, may cause serious interference if the decomposition solution is used directly for the determination of trace elements by a polarographic method, *e.g.*, anodic stripping voltammetry (ASV), or differential pulse polarography (DPP).[16,17] These interferences may be traced to organic fragments, as can be shown by a cyclic voltammogram (Fig. 8), where irreversible cathodic peaks occur.

Direct-current polarography provided the first clues to the occurrence of such organic fragments. Since the heights of the polarographic waves are proportional to the amounts of the residues, the polarographic activity of the solution could be correlated with the temperature and the time of the decomposition. As exemplified by milk powder (Fig. 9) the concentration of the organic fragments was found to be constant at temperatures ≤160°, even if long decomposition times were used (this diagram is intended only to show that the concentration of the organic residues in the decomposition solution decreases with increasing temperature). Direct-current polarography is not sensitive enough to detect traces of such organic fragments. The experiments show, however, that the production of interfering components, and the time needed for the decomposition, depend strongly on temperature as well as on the

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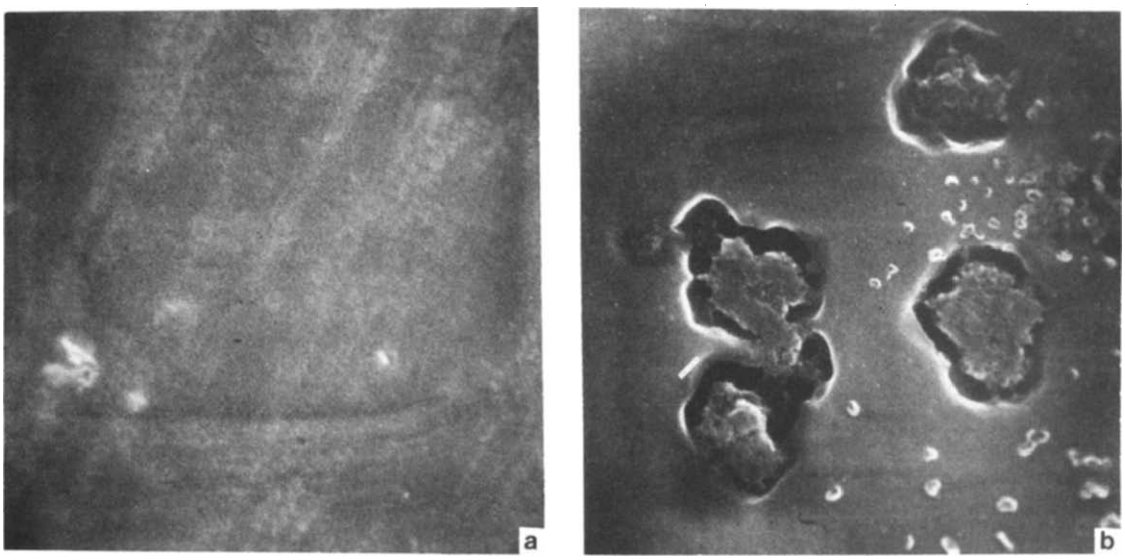

Fig. 5. Alteration of a SIGRADUR G® surface by thermal treatment with HNO_3 (70%): (*a*) untreated surface (SEM 300 ×, angle 0°); (*b*) treated surface, pressure decomposition conditions (160°C, 10 hr), (SEM 1000 ×, angle 0°).

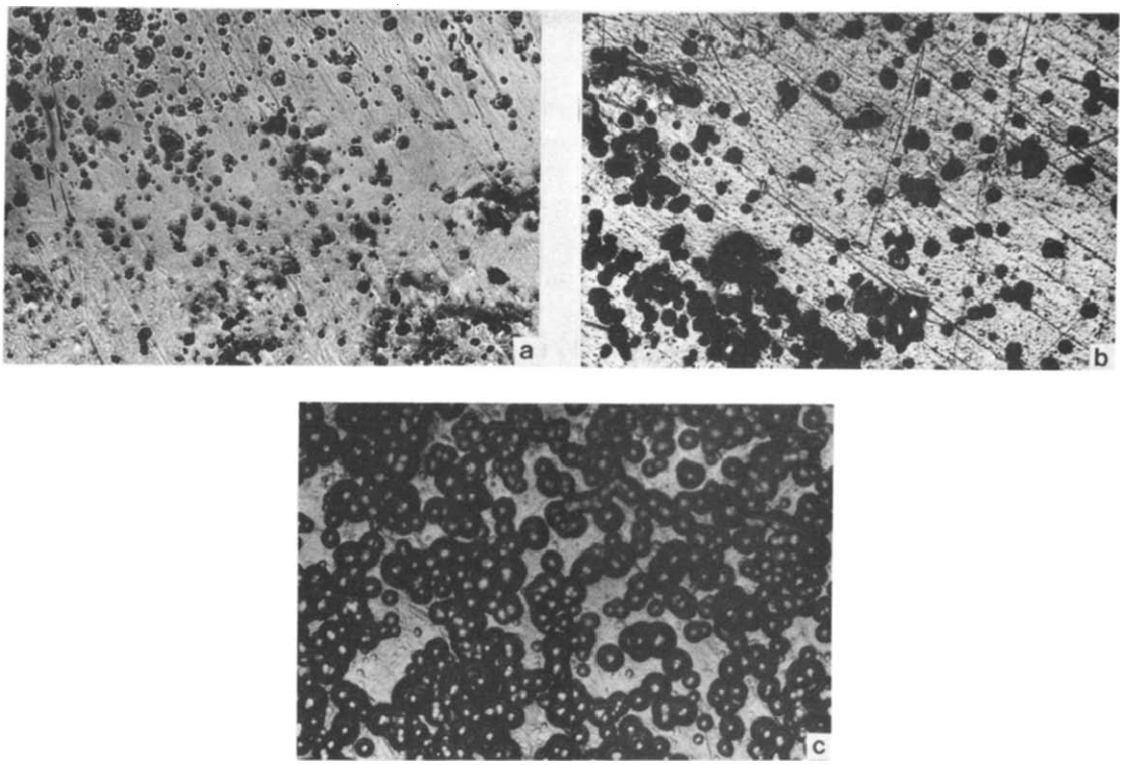

Fig. 6. Alteration of a SIGRADUR G® surface by thermal treatment with HNO_3 (70%) (light-microscope 200 ×): (*a*) untreated; (*b*) treated surface, pressure decomposition conditions (160°C, 24 hr), (*c*) treated surface, pressure decomposition conditions (160°C, 96 hr).

nature of the matrix. Matrices consisting mainly of carbohydrates and natural fats, *e.g.*, hay or cattle tallow respectively, give less difficulty than those with a high protein content, *e.g.*, liver, blood sera and milk powder.

The appearance of interferences as a function of amount of sample decomposition temperature, and concentration of nitric acid, can be shown more clearly by ASV (Fig. 10a). The application of nitric acid (100% w/v) resulted in too high a pressure in the vessel, causing blow-off of the solution. Moreover, purification of nitric acid with a concentration higher than 70% w/v by sub-boiling point distillation is impossible.

The higher the concentration of the organic fragments, the higher is the cathodic current. Not only these components cause interferences, but also nitrous fumes dissolved in the decomposition solution. Though these gases

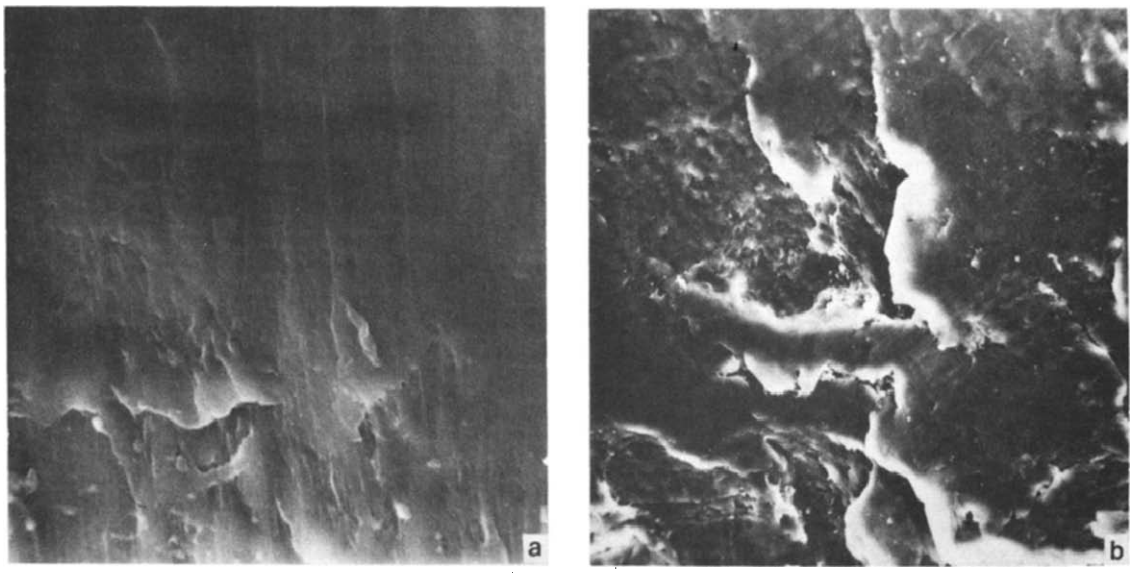

Fig. 7. Alteration of a PTFE surface by thermal treatment with HNO_3 (70%): (*a*) untreated surface (SEM 3000×, angle 0°); (*b*) treated surface, pressure decomposition conditions (160°C, 10 hr) (SEM 1000 ×, angle 0°).

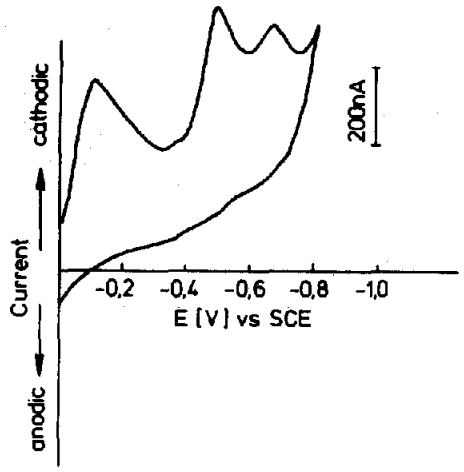

Fig. 8. Cyclic voltammogram of a decomposition solution (0.1 g of serum, 0.5 ml of HNO_3 (70%), 200°C, 5 hr), starting potential 0 V *vs.* SCE, scan-rate 50 mV/sec.

partly diffuse through PTFE they remain within the glassy carbon vessel, as indicated by the yellow colour of the decomposition solution. This interference can, however, be eliminated by evaporating the solution to dryness and taking up the residue with 0.1*M* hydrochloric acid (Fig. 10b).

The more sensitive differential pulse anodic stripping voltammetry (DPASV) illustrates clearly the extent to which the determination of Cu, Cd, Pb *etc.* in blood serum is interfered with (Fig. 11). It was found impossible to determine any of the three elements in, *e.g.*, blood serum, because the sensitivity was not high enough for a small fraction of the decomposition solution to be used, and even with only 300 μl of the 2 ml of solution (*i.e.*, 15% of the 0.1 g of serum taken as sample) there was strong interference. This means that even a decomposition temperature of 200° is not high enough if the trace elements are to be determined directly in the decomposition solution by a polarographic method.[18]

The situation may be improved, however, if the solution is fumed with 0.2 ml of perchloric acid (60% w/v). No losses of Cd and Pb then occur (Fig. 12). If the decomposition is followed by such a fuming step, a decomposition temperature of 160° is sufficient. The fuming can be done directly in the decomposition vessel with a special heating device (Fig. 13). This method, however, carries the risk

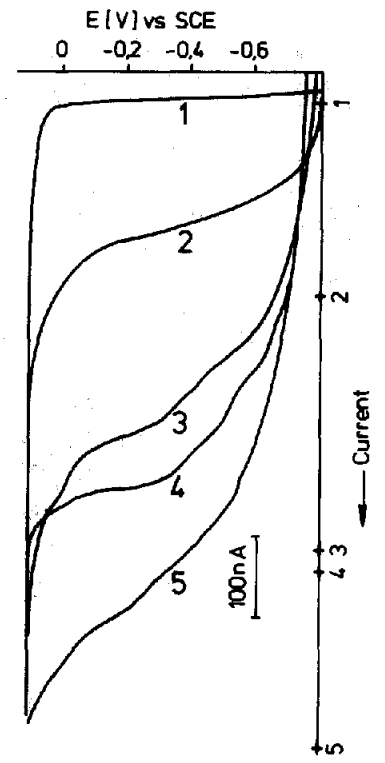

Fig. 10*a*. Anodic stripping voltammograms of decomposition solutions. Current as a function of sample weight (serum), decomposition temperature, and acid concentration: 50-μl aliquots from the total (2 ml) were used. *1*—blank (HNO_3, 70%, 200°C, 5 hr), *2*—0.1 g (0.5 ml of HNO_3, 70%, 200°C, 5 hr), *3*—0.2 g (0.5 ml of HNO_3, 70%, 200°C, 5 hr), *4*—0.1 g (0.5 ml of HNO_3, 85%, 200°C, 5 hr), *5*—0.1 g (0.5 ml of HNO_3, 70%, 160°C, 5 hr).

of both losing easily volatilized elements such as Se, Te and Cr (as CrO_2Cl_2) and of contaminating the decomposition solution unless comprehensive conditions of cleanliness are met, *e.g.*, glove boxes or clean benches which reduce the level of blanks.[1,2]

A decomposition with acid mixtures containing perchloric acid, *e.g.*, $HNO_3/H_2SO_4/HClO_4$ (2:1:1) would

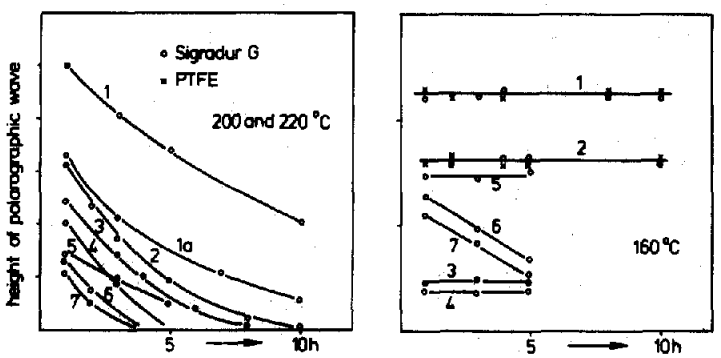

Fig. 9. Detection of organic fragments in the decomposition solution by d.c. polarography (supporting electrolyte: borax-buffer pH = 9.3, half-wave potential of the irreversible wave between −0.5 and −0.7 V *vs.* SCE) after pressure decomposition of different organic substances with 0.5 ml of HNO_3 (70%) at different temperatures. *1*—milk powder (60 mg), *1a*—milk powder (60 mg, 220°C), *2*—liver (100 mg), *3*—bone (60 mg), *4*—serum (100 mg), *5*—protein concentrate (50 mg), *6*—hay (60 mg), *7*—cattle tallow (100 mg).

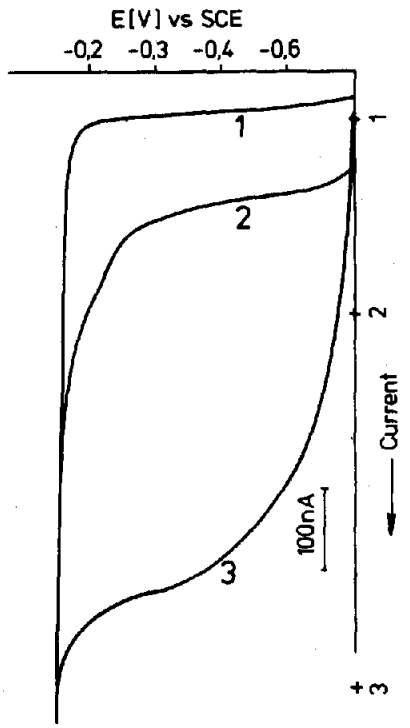

Fig. 10*b*. Anodic stripping voltammograms of a decomposition solution (0.1 g of serum, 0.5 ml of HNO_3, 70%, 200°C, 5 hr) before and after evaporation: 50-μl aliquots from the total (2 ml) were used. *1*—blank, *2*—after evaporation, *3*—before evaporation.

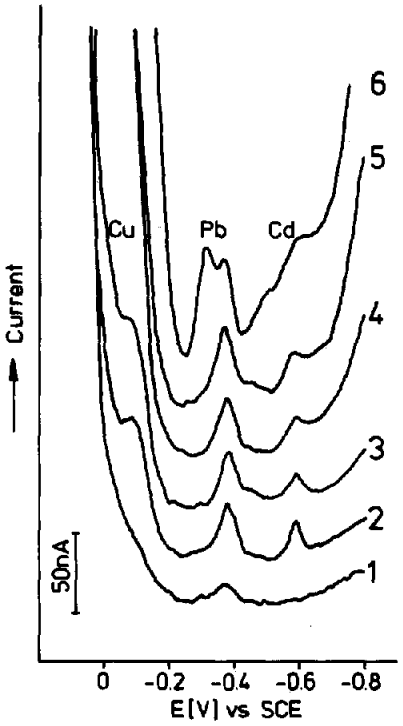

Fig. 11. Differential pulse anodic stripping voltammograms of a decomposition solution (0.1 g of serum, 0.5 ml of HNO_3, 70%, 5 hr) spiked with 2 ng of Cd, 2 ng of Pb, 5 ng of Cu. Aliquots from the total (2 ml) were used. *1*—blank, *2*—standard solution, *3*—10 μl, *4*—50 μl, *5*—100 μl, *6*—300 μl.

have a sufficiently high oxidation potential at 200° to mineralize organic matter completely, but there is a considerable explosion hazard as we have ourselves experienced in the case of the decomposition of an aromatic compound with this mixture (Fig. 14).[19]

Incomplete decomposition of organic matrices causes less interference if atomic spectroscopic determination methods, *e.g.*, AAS, OES and XRF, are used after a pressure-bomb decomposition. Strong interferences may still occur, however, if electrothermal AAS is used.

Another possibility for remedying the situation is the classical decomposition in a fused quartz tube according to Carius.[20] By this method it can be established that at 250° the oxidation potential of nitric acid (70% w/v), under the stated conditions, is high enough to yield a solution without measurable polarographic activity (Fig. 15). However, fusing the quartz tube and opening the ampoule, which is under pressure, require skill and time; moreover, the danger of explosion is relatively large.[21] Furthermore, hydrofluoric acid cannot be used. Chloric acid, which has a higher oxidation potential than nitric acid, can be used to good effect at 200° (Fig. 15). A mixture of 20% chloric acid and 7% perchloric acid is commercially available*, which allows handling without risk. Even with this mixture, milk powder cannot be completely decomposed under these conditions. Fuming of the decomposition solution with perchloric acid (60% w/v) is still necessary (Fig. 16).

The sample weight should generally be limited to about 200 mg. Exceptions may be possible, but ought to be tested for the matrix in question, to avoid too violent a decomposition causing mostly blow-off of vapour. Although our

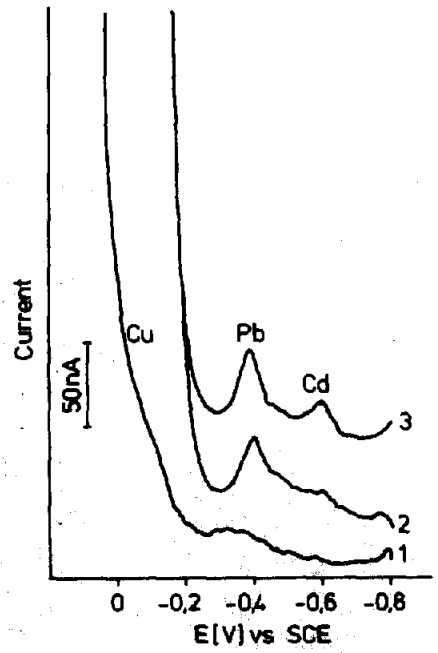

Fig. 12. Differential pulse anodic stripping voltammograms of a decomposition solution (0.1 g of serum, 0.5 ml of HNO_3, 70%, 200°C, 5 hr) after evaporation with $HClO_4$, 60%: *1*—blank, *2*—sample, *3*—sample spiked with 1 ng of Cd and 1 ng of Pb.

* Item No. 10741, E. Merck AG, D-6100 Darmstadt, FRG.

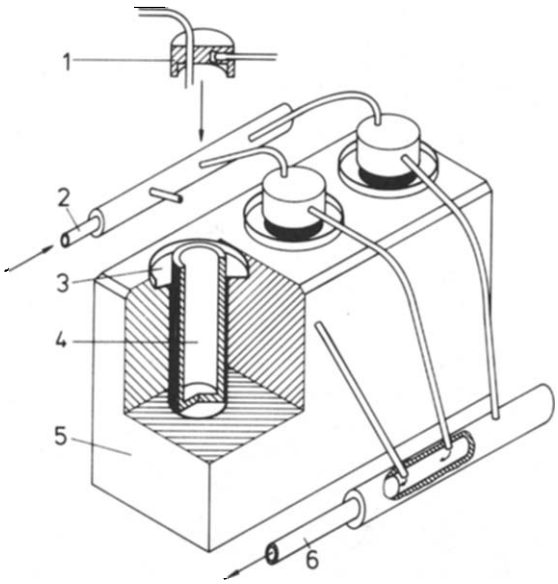

Fig. 13. Arrangement for the evaporation of solutions. *1*—PTFE lid, *2*—carrier gas, *3*—PTFE protection mantle, *4*—decomposition vessel, *5*—Al heating block, *6*—condensate outlet.

system has been tested for safety with explosives[22] to make sure that under normal conditions accidents should not occur, there is no convincing reason for the application of sample quantities ≥ 200 mg, since with a sample of this size all trace elements can easily be determined in the low ng/g range by the common methods.

A source of error inherent in the opening of the pressure bomb must be pointed out. On account of the high impermeability of glassy carbon to gases there is still a positive pressure in the vessel after the decomposition, and its magnitude depends upon the nature and amount of the sample. When the cover of the bomb is unscrewed, a bit of acid vapour blows off, which may pick up traces of Fe, Cr, Ni, V, Mo—the components of the stainless steel—by contact with the wall of the bomb case. The vapour condenses partly on the wall of the bomb and on the rim of the decomposition vessel. The droplets spilled into the vessel, even though only some μl in volume, contaminate the decomposition solution (Table 4), and this shows up in ultratrace analysis. Therefore careful manipulation is important when rinsing the upper part of the vessel for quantitative transfer of the solution to other apparatus. It is possible to eliminate these interferences by enveloping the upper external part of the vessel and its lid in a piece of high-purity aluminium foil or sheathing the internal wall of the bomb with a PTFE film by means of a PTFE spray, before starting the decomposition procedure.

In this connection it has to be mentioned that the walls of the bomb must be free from any corrosion products, which may easily come off and arrive in the decomposition vessel, greatly contaminating the solution. The bomb may easily be cleaned with concentrated phosphoric acid at room temperature by a prolonged soaking (about 10 hr), followed by careful rinsing with doubly distilled water and acetone.

Investigations with tracers (^{74}As, ^{75}Se, ^{203}Hg) proved that no losses greater than 5% occurred because of lack of tightness of the decomposition vessel or because of loss of solution when the bomb was opened. The latter losses can be reduced to $\leq 1\%$ if the bomb is cooled to about $-20°$ by immersing it briefly in liquid nitrogen before opening the bomb case, to reduce the overpressure in the vessel. When the decomposition solution has to be transferred from the decomposition vessel to other apparatus the use of pipettes fitted with a suction system can be recommended. The vessel must subsequently be rinsed with about 0.5–1.0 ml of nitric acid (70% w/v), or losses of up to 8% may occur, even though glassy carbon is hardly wettable.

Procedure

The assembly is the same as that already described.[5] Arrangements consisting of 3 or 10 bombs are commercially available. In place of the PTFE vessel, one made

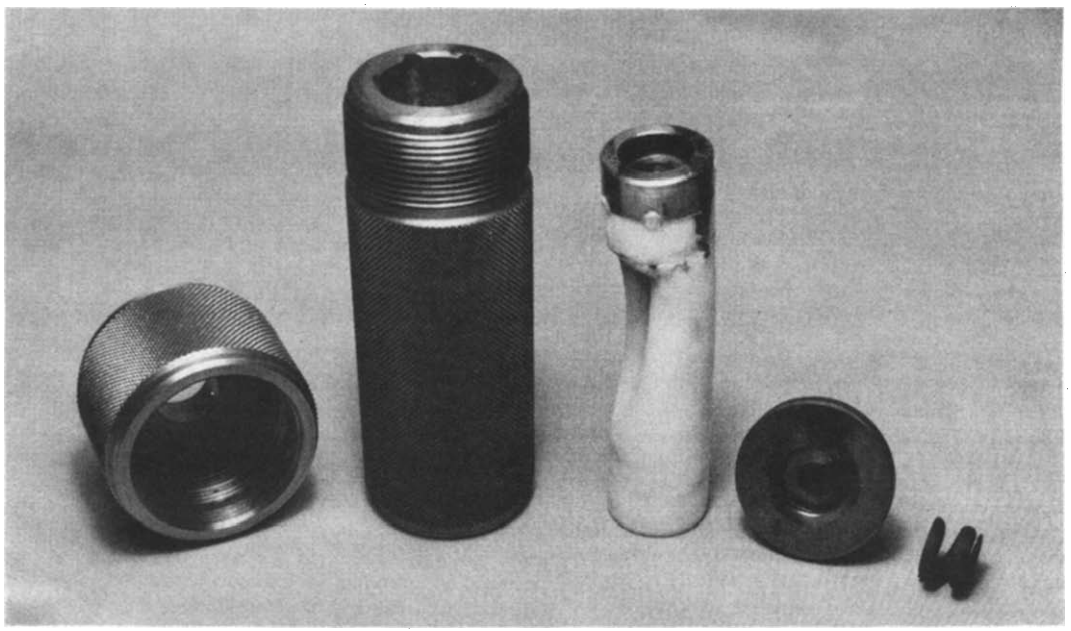

Fig. 14. A PTFE vessel after a pressure decomposition of an organic compound at 170°C with a mixture of 0.2 ml of HNO_3 (70%) and 0.6 ml of $HClO_4$ (60%).

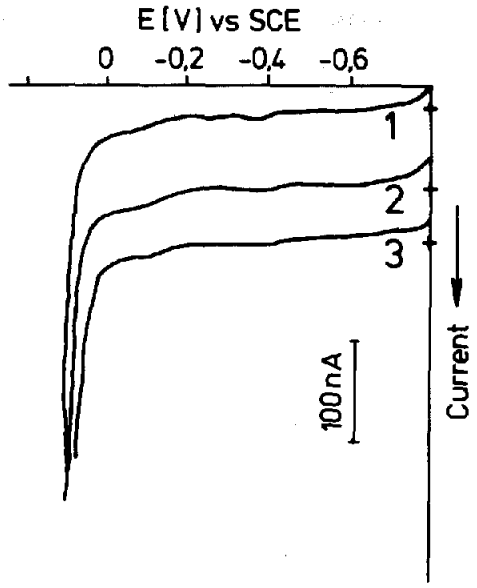

Fig. 15. Anodic stripping voltammograms of different decomposition solutions (0.1 g of serum). *1*—blank, *2*—fused quartz ampoule (0.5 ml of HNO_3, 70%, 250°C, 5 hr), *3*—glassy carbon vessel (0.5 ml of $HClO_3$, 20%/$HClO_4$, 7%, 200°C, 5 hr).

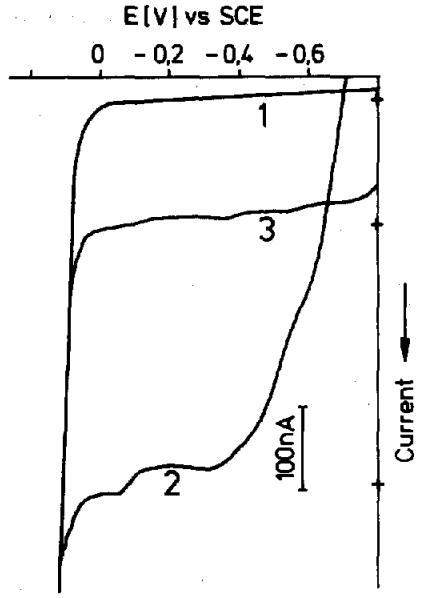

Fig. 16. Anodic stripping voltammograms of a decomposition solution of milk powder (50 mg, 0.5 ml of $HClO_3$, 20%/$HClO_4$, 7%, 200°C, 5 hr). *1*—blank, *2*—directly used, *3*—after evaporation with 0.25 ml of $HClO_4$ (60%).

of glassy carbon (Fig. 1) is used (volume 17 ml, height with lid 85 mm, outer diameter 25 mm, wall thickness 3 mm). Since the thickness of the lid is also only 3 mm—depending on the preparation process—a supporting disk is necessary in order to avoid the risk of breakage of the lid. Graphite–PTFE has proved suitable for that. The bottom side of the lid is sheathed with a PTFE foil (1 mm thick). Also a PTFE ring made of special PTFE foil* (outer diameter 24 mm, inner diameter 18 mm, thickness 0.4 mm) is used, which has to be steamed with nitric acid (70% w/v) to remove detritus from the punch (Table 4), and to ensure absolute sealing it has to be replaced after each decomposition. A spring (spring constant ~100 kg/mm) presses the lid tightly on the vessel, thus forming a safety-valve, which allows blowing-off of vapour (if the pressure becomes too high) through notches milled in the bomb case. At the bottom of the bomb a PTFE disk (2 mm) should be inserted to offset any slight unevenness of the vessel bottom, in order to obviate the risk of breakage while screwing on the cover of the bomb.

The weight of the sample to be decomposed depends on its nature. Table 5 shows the maximum sample weights and the time required for the decomposition. Radionuclides of the easily volatilized elements As, Se, Hg were used to check recoveries by the technique. The yields lay in the region of ≥97%.

A special spanner* is used to be sure of the vessel being tight during the decomposition. The bomb is heated in an aluminium or brass block with time and temperature control. A programmable controller ensures matching the heating rates to the matrix in question.

* Forschungsinstitut Berghof, D-7400 Tübingen-Lustnau, FRG.

Table 4. Introduction of contaminants by the stainless-steel bomb in the decomposition of organic matrices with 0.5 ml of nitric acid (70%) in PTFE and SIGRADUR G® vessels

	Concentrations of impurities, *ng/2 ml*			
	SIGRADUR G®		PTFE	
Element	decomposition without matrix	decomposition with matrix and rinsing of the rim	decomposition without matrix	decomposition with matrix and rinsing of the rim
Cd*	<0.5	3–9	0.5	<20
Co	<5	10–40	<5	<30
Cu*	<5	500–1000	<5	<900
Cr	<5	<40		
V	<10	<20		
Fe	10	<700		<1000
Mn	<1	<80	<1	<200
Ni	<5	<300	<5	<1000
Mo	<5	<50	<5	<50

* The high blanks may be due to the punch used for cutting the PTFE seal ring.

Table 5. Decomposition parameters for some organic matrices

Matrix	Sample weight, *mg*	Decomposition acid, *ml*	Heating time, *hr*			Heating period at 200°C, *hr*
			80°C	140°C	200°C	
Pork bones	200	0.5 HNO_3	—	—	0.5	1
Milk powder	100	0.5 HNO_3	—	—	1	2
Hair (human)	50	0.5 HNO_3	1	0.5	0.5	2
Cattle tallow	100	0.5 HNO_3	—	—	0.5	1
Grass	60	0.5 HNO_3/0.2 HF	1	1	0.5	0.5
Hay	60	0.5 HNO_3/0.2 HF	1	1	0.5	0.5
Liver	200	0.5 HNO_3	0.5	0.5	0.5	2
Serum	200	0.5 HNO_3	0.5	0.5	0.5	2.5
Protein-concentrate	50	0.5 HNO_3	1.0	0.5	0.5	2.5
Pine needle	50	0.5 HNO_3	0.5	0.5	0.5	0.5

The maximum temperature must not exceed 220°. After the decomposition the bomb is cooled down either in the air or, for ultratrace analysis, with liquid nitrogen. The solution in the vessel is taken up with an appropriate pipette for analysis. Further manipulations, *e.g.*, preconcentration and separation, can be done in the same vessel.[23] Droplets on the rim of the vessel are disregarded.

The d.c. polarographic investigations were carried out with the Polarocord E 246 (dropping mercury electrode and SCE) (Metrohm, Herisau, Switzerland). ASV, DPASV and cylic voltammetry were conducted with a Multipolarograph, Type Amel 471 (Erbe Elektromedizin, D-7400 Tübingen, FRG), with the following experimental conditions. Electrodes: hanging mercury electrode and SCE. Electrolyte: 0.1 *M* hydrochloric acid. Volume of electrolyte: 3 ml. Deaeration time: 10 min with argon (99.998% pure). In DPASV the modulation amplitude was 20–50 mV. Further details of the polarographic investigations are given in the legends of the individual figures.

DISCUSSION

The decomposition of many organic substances by nitric acid with a concentration of $\leq 85\%$ w/v, under pressure in PTFE vessels at temperatures up to 160°, is found to be incomplete. The remaining organic fragments interfere with the determination of trace elements if the decomposition solution is used directly for their determination by a polarographic method, *e.g.*, ASV or DPASV. Investigations with fused glass ampoules have shown that a temperature of at least 250° is necessary to decompose organic matter with nitric acid (70% w/v) to such an extent that the decomposition solution shows no polarographic activity. Since the poor thermal stability of PTFE allows a decomposition temperature of only about 170° under pressure conditions, a new vessel made of glassy carbon (Sigradur G®) has been tested, with which a temperature of up to about 220° can be used. The temperature-limiting factor is the sealing. At present, there is no material available for this purpose which stands a temperature $\geq 220°$. It is therefore necessary to resort to various expedients to obviate interferences due to organic fragments contained in the decomposition solution, if a polarographic determination method is to be applied. The following means are possible.

1. The decomposition solution is evaporated to fumes with perchloric acid. A decomposition time of 5 hr at 160° is sufficient. For the evaporation (200°), the solution has to be transferred to a quartz receptacle if a PTFE vessel is used for the decomposition. This additional step is, however, subject to the risk of introduction of contamination.

2. For the decomposition, chloric acid (20% chloric acid/7% perchloric acid), which has a higher oxidation potential than nitric acid, is used. Normally a decomposition time of 3 hr at 200° is sufficient to decompose the substance sufficiently for the remaining organic fragments to be mineralized by heating with perchloric acid (60% w/v). For the sensitive and accurate determination of those trace elements which can be determined by the quoted polarographic methods, the decomposition solution has to be evaporated and the residue dissolved in an appropriate electrolyte (*e.g.*, 0.1 *M* hydrochloric acid for the determination of Cd and Pb). There are, however, organic substances, *e.g.*, milk powder, which cannot be completely mineralized under these conditions even if long decomposition times are used.

3. Another possibility is decomposition in fused quartz tubes, but this technique is not suited for routine work.

General conclusions cannot be drawn from these experiences gained in the decomposition of only a few matrices. The choice for the appropriate decomposition technique depends on the sample to be decomposed, and on the method to be applied for the determination of the trace elements in question.

Acknowledgements—We are indebted to the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg for sponsoring this work, and to Sigri Elektrographit GmbH, Meitingen bei Augsburg, FRG, for providing the glassy carbon vessels.

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VERGLEICHENDE UNTERSUCHUNG AN REAGENTIEN ZUR SPEKTRALPHOTOMETRISCHEN BESTIMMUNG VON ZINK

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Zusammenfassung—Mit Hilfe eines Bewertungsschemas werden bekannte Verfahren zur photometrischen Zinkbestimmung mit den Reagentien 4-(2-Pyridylazo)-resorcin, 4-(2-Thiazolylazo)-resorcin, 1-(2-Pyridylazo)-2-naphthol, 1-(2-Thizolylazo)-2-naphthol, Sulfarsazen, Zincon, Xylenolorange und 8-Hydroxychinolin getestet und kritisch eingeschätzt.

Die Zahl der Publikationen auf dem Gebiet der Spektralphotometrie hat in den letzten Jahren sprunghaft zugenommen. Wegen der unkritischen Natur vieler Veröffentlichungen sind jedoch die Vor- und Nachteile einer vorgestellten Methode oft nicht klar erkennbar. Ein objektiver Vergleich der Reagentien bzw. der Verfahren zur Bestimmung eines Elementes untereinander ist durch das Fehlen international einheitlicher Bewertungskriterien und verbindlicher Kennzahlen meist nicht möglich. Mit diesen Schwierigkeiten ist der Analytiker in der Praxis konfrontiert, wenn er aus einem großen Reagentienangebot das für seine spezielle Zielstellung günstigste Reagens auswählen muß. Um dabei Mißgriffen vorzubeugen, ist eine präzise Charakterisierung erforderlich, die allerdings umfangreiche und zeitaufwendige Voruntersuchungen notwendig macht.

Wir haben ein Bewertungsschema erarbeitet, nach dem vorgegangen werden sollte, um photometrische Verfahren miteinander zu vergleichen.[1] Alle Angaben und Kennzahlen, die zur Charakterisierung des Verfahrens notwendig sind, können danach in tabellarischer Form übersichtlich und leicht vergleichbar dargestellt werden. An dieser Stelle sei auch auf eine entsprechende Empfehlung von Kirkbright[2] zu diesem Thema hingewiesen.

Nach unseren Erfahrungen sollte sich die Untersuchung in drei Teile gliedern.

1. Charakterisierung des Reagens—darunter sind Angaben zur Herkunft und Reinheit des Reagens zu verstehen.

2. Charakterisierung der der photometrischen Bestimmung zugrundeliegenden Farbreaktion—darunter fällt die Wahl der entsprechenden Reaktionsbedingungen wie pH-Wert, Puffer, Reagenskonzentration, Gesamtelektrolytkonzentration und zeitliche Stabilität der Farblösung.

3. Charakterisierung der Methode—dazu gehören die Kennzahlen, die es gestatten, Verfahren miteinander zu vergleichen. Diese unfassen den Arbeitsbereich, die Gleichung der Eichgeraden, die Empfindlichkeit, die Reproduzierbarkeit und die theoretische Grenze des Verfahrens, ausgedrückt durch die Nachweisgrenze nach Kaiser.[3]

Der Selektivität des Verfahrens, die durch eine Maßzahl nur schwer auszudrücken ist, muß besondere Beachtung geschenkt werden. Wir prüften den Einfluß von Fremdionen bis höchstens zu einem 100-fachen Überschuß. Das ist eine willkürliche Festlegung, um den ohnehin schon sehr großen Arbeitsaufwand bei diesen Untersuchungen zu minimieren. Weiterhin legten wir fest, daß ein Stoff dann stört, wenn seine Anwesenheit eine Extinktionsänderung von mehr als dem absoluten Streubereich $T(S)$ (für $S = 99\%$) hervorruft.

Bei dem vorgeschlagenen Bewertungsschema verfolgten wir das Ziel, konkrete Festlegungen zu treffen, die es gestatten, photometrische Analysenverfahren objektiv beurteilen und vergleichen zu können. Mit Hilfe dieses Schemas haben wir den Versuch gemacht, bekannte Verfahren zur photometrischen Zinkbestimmung kritisch zu bewerten, da die bisher veröffentlichten Zusammenstellungen unvollständig, uneinheitlich und wenig kritisch sind. Dazu wurden aus einer großen Anzahl empfohlener Reagentien die allen Anschein nach zweckmäßigsten ausgewählt.

Folgende Reagentien wurden untersucht:

4-(2-Pyridylazo)-resorcin
4-(2-Thiazolylazo)-resorcin
1-(2-Pyridylazo)-2-naphthol
1-(2-Thiazolylazo)-2-naphthol
Sulfarsazen
Zincon
Xylenolorange
8-Hydroxychinolin

Im weiteren sind die Untersuchungsergebnisse für die einzelnen Reagentien dargestellt. Die wichtigsten Informationen und Kennzahlen sind in den Tabellen 1-3 zusammengefaßt. Im jeweiligen Abschnitt "Ergebnisse" sind die Resultate nur kommentiert, für alle anderen Angaben wird auf die Tabellen verwiesen.

Tabelle 1. Charakterisierung des Reagens

Namen und Quelle	Lösung	Elementaranalyse*	DC-Test†	ϵ_λ, $l \cdot mole^{-1} \cdot cm^{-1}$
4-(2-Pyridylazo)-resorcin PAR $C_{11}H_8N_3NaO_2 \cdot H_2O$ Chemapol (Charge 2031062)	in H_2O Haltbarkeit >1 Monat	C 48,0% (51,8) H 3,9% (3,9) N 13,5% (16,4)	keine Verunreinigung festellbar	$\epsilon_{415} = 2{,}62 \cdot 10^4$
4-(2-Thiazolylazo)-resorcin TAR $C_9H_6N_3NaO_2S$ Chemapol (Charge 80276568)	in CH_3OH Haltbarkeit >1 Monat	C 48,0% (44,4) H 3,3% (2,5) N 16,6% (17,3) S 14,3% (13,2)	keine Verunreinigung feststellbar	$\epsilon_{482} = 2{,}45 \cdot 10^4$
1-(2-Pyridylazo)-2-naphthol PAN $C_{15}H_{11}N_3O$ Berlin-Chemie	in C_2H_5OH Haltbarkeit >1 Monat	C 70,4% (72,0) H 4,0% (4,0) N 16,3% (17,0)	keine Verunreinigung feststellbar	$\epsilon_{300} = 1{,}3 \cdot 10^4$ $\epsilon_{465} = 1{,}7 \cdot 10^4$
1-(2-Thiazolylazo)-2-naphthol TAN $C_{13}H_9N_3OS$ Chemapol	in CH_3OH Haltbarkeit >1 Monat	C 61,0% (61,2) H 3,6% (3,6) N 16,3% (16,5)	keine Verunreinigung feststellbar	$\epsilon_{535} = 2{,}1 \cdot 10^4$ $\epsilon_{575} = 4{,}7 \cdot 10^4$
Sulfarsazen 4-Nitro-2-arsono-benzol-1,4'-diazoamino-1',1''-azobenzol-4''-sulfonsäure, Na-Salz $C_{18}H_{14}N_6AsNaO_8S$ Sojuschimexport	in $Na_2B_4O_7$-Lösung Haltbarkeit >1 Monat	C 39,4% (37,8) H 3,4% (2,5) N 13,1% (14,6)	keine Verunreinigung feststellbar	$\epsilon_{415} = 3{,}8 \cdot 10^4$
Zincon 2-Carboxy-2'-hydroxy-5'-sulfoformazylbenzol $C_{20}H_{16}N_4O_6S$ Chemapol (Charge 91102/0871)	in C_2H_5OH Haltbarkeit 3 Wochen	C 63,1% (54,6) H 4,3% (3,6) N 11,4% (12,7) S 2,3% (7,3)	keine Verunreinigung feststellbar	$\epsilon_{356} = 3{,}2 \cdot 10^4$ $\epsilon_{530} = 0{,}4 \cdot 10^4$
Xylenolorange 3,3'-Bis-*N*,*N'*-di(carboxy-methyl)-aminmethyl-o-kresol sulfophthalein $C_{31}H_{32}N_2O_{13}S$ Chemapol Charge 90025170)	in C_2H_5OH/H_2O Haltbarkeit 3 Wochen	C 45,0% (55,0) H 4,8% (4,9) N 3,9% (4,2)	4 Komponenten	$\epsilon_{205} = 2{,}6 \cdot 10^4$ $\epsilon_{273} = 0{,}8 \cdot 10^4$ $\epsilon_{436} = 1{,}4 \cdot 10^4$
8-Hydroxychinolin C_9H_7NO Laborchemie Apolda (Charge 80294)	in $CHCl_3$ bzw. in Di-chloräthan Haltbarkeit >1 Monat	C 74,4% (74,4) H 4,8% (4,8) N 6,5% (6,6)	keine Verunreinigung feststellbar	$\epsilon_{245} = 3{,}4 \cdot 10^5$

*In Klammern die theoretischen Gehalte.
†Dünnschichtchromatographie.

Tabelle 2. Charakterisierung der Reaktion

Reagens	λ_{max} *nm*	pH-Wert	Puffer	Ionenstärke	Reagenskonz., *μM*	Stabilität, *min*	Extraktionsmittel
PAR	R: 415* K: 495	7,5–10,0	Borat pH 9,0	bis 1,0 ohne Einfluß	3,9	> 60	—
TAR	R: 475 K: 530	7,0–8,5	Triäthanolamin/NaOH pH 7,5	bis 1,0 ohne Einfluß	4,5	> 60	—
PAN	R: 470 K: 560	6,5–10,0	NaAc–HAc pH 6,5	bis 1,0 ohne Einfluß	4,0	bis 60	$CHCl_3$ 60 sec
TAN	R: 485 K: 585	7,0–7,5	NaAc/HAc pH 7,0	bis 1,0 ohne Einfluß	3,0	bis 30	$CHCl_3$ 60 sec
Sulfarsazen	R: 420 K: 505	9,0–10,0	Borat pH 9,5	≤ 0,05	3,5	bis 60	—
Zincon	R: 490 K: 625	8.5–9,25	Borat pH 9,0	bis 1,0 ohne Einfluß	12	> 60	—
Xylenolorange	R: 435 K: 575	5,5–6,0	NaAc/HAc pH 6,0	≤ 0,02	5,0	bis 45	—
Oxin/n-Butylamin	R: — K: 400	10,0–12,0	—	bis 1,0 ohne Einfluß	30	> 60	$CHCl_3$ 60 sec
Oxin/$HClO_4$	R: — K: 365	5,0–6,0	NaAc/HAc pH 5,7	~ 0,9	150	> 60	Dichloräthan 120 sec

* R = Reagens.
† K = Komplex.

Wegen der großen Bedeutung des Einflusses von Fremdionen auf die Bestimmungsverfahren ist der Selektivität jeweils ein gesonderter Abschnitt gewidmet.

BESTIMMUNG VON ZINK MIT 4-(2-PYRIDYLAZO)-RESORCIN

4-(2-Pyridylazo)-resorcin (PAR) wurde erstmalig als Reagens zur photometrischen Zink bestimmung von Kitano[4] beschrieben. Der sich bei pH 9,7 maximal bildende Komplex hat ein Absorptionsmaximum bei 493 nm. Nonova und Mitarbeiter[5] bestimmten Zink mit PAR extraktions-photometrisch in Gegenwart von Cetyldimethylammoniumchlorid. Breite Anwendung findet das Reagens als Indikator zur komplexometrischen Bestimmung von Wismut, Cadmium, Kupfer, Blei sowie Zink.[6] Der sich bei pH > 5,2 bildende Komplex weist nach Angaben von Sommer[6] ein Metall:Ligand-Verhältnis von 1:2 auf. Iwamoto[7] verwendete PAR zur Tüpfelanalyse von Schwermetallkationen in alkalischer Lösung.

Experimenteller Teil

Geräte und Reagentien. Die photometrischen Messungen wurden mit dem Spektralphotometer VSU 2 des VEB Carl Zeiss Jena ausgeführt; für die Aufnahme von Absorptionsspektren stand das registrierende Spektralphotometer Specord UV–VIS der gleichen Firma zur Verfügung. Die pH-Werte wurden am pH-Meter MV 85 der Firma Clamann und Grahnert, Dresden, gemessen.

PAR-Lösung: 0,05 %ig in Wasser ($=1{,}96\cdot10^{-3}M$).

Puffer-Lösung: pH 9,0 (0,1*N* Natriumtetraboratlösung wird mittels 0,1*M* Saltsäure auf pH 9,0 eingestellt).

Arbeitsvorschrift. Zu der zinkhaltigen Probelösung (Zn-Gehalt bis 45 µg) gibt man im 50-ml Maßkolben 20 ml Puffer- sowie 2 ml PAR-Lösung und füllt mit Wasser zur Marke auf. Die Messung erfolgt sofort bei 495 nm in 1-cm Küvetten gegen eine Reagentienblindlösung.

Ergebnisse

Bemerkungen zum Verfahren. Eine Zusammenstellung der Kennzahlen zur Bestimmung von Zink und PAR enthalten die Tabellen 1–3. Der Zink–PAR-Komplex ist bei pH 7 voll ausgebildet und bis in den alkalischen Bereich beständig. Am günstigsten arbeitet man bei pH 9,0 unter Verwendung eines Boratpuffers.

Von Vorteil ist die große Stabilität des Komplexes, die nur einen geringen Überschuß an Reagens und keine exakt eingestellte Ionenstärke erfordert. (Blindwert bei *ca.* 5-fachem molarem Reagensüberschuß, $E = 0{,}12$.) Da auch die zeitliche Stabilität des Komplexes gegeben ist, erweist sich das Verfahren zur photometrischen Zinkbestimmung als recht geeignet.

Der Extinktionskoeffizient ist mit $\epsilon_{495} = 8{,}7\cdot10^4$ $l\cdot mole^{-1}\cdot cm^{-1}$ sehr hoch und stimmt mit den Angaben der Literatur überein [$\epsilon_{495} = 8{,}68\cdot10^4$ (Kirkbright)[2] bzw. $6{,}3\cdot10^4$ (Kitano und Ueda)[4]].

Der p*D*-Wert der Nachweisreaktion von Zink mit PAR beträgt 5,4 bei pH 9.

Selektivität des Verfahrens. Unter den angegebenen Bedingungen reagieren folgende Ionen nicht mit dem Reagens und können mindestens bis zum 100-fachen Überschuß (100-fach stellt die Untersuchungsgrenze dar) vorhanden sein: Al(III), As(III), Ba(II), Cr(III, VI), Ge(IV), K(I), Li(I), Mo(VI), Na(I), Pt(IV), Rb(I), Re(VII), Sb(V), Se(IV), Sr(II), Te(VI), Tl(I), W(VI).

Folgende Ionen stören die Bestimmung entweder durch gleiche Reaktion mit PAR oder durch Ausfallen der Hydroxide:

ab 1:50 Au(III), Bi(III), Ca(II), In(III), La(III), Nb(V), Rh(III), Sn(II, IV), Zr(IV);
ab 1:25 Ce(III, IV), Ir(IV), Os(VIII), Th(IV);
ab 1:10 Mg(II), V(V);
ab 1:5 Ag(I), Ga(III), Pd(II), Ta(V), Y(III);
in jedem Verhältnis Be(II), Cd(II), Co(II), Cu(II), Fe(II, III), Hg(II), Mn(II), Ni(II), Pb(II), Ru(III), Sc(III), Ti(IV), U(VI).

BESTIMMUNG VON ZINK MIT 4-(2-THIAZOLYLAZO)-RESORCIN

4-(2-Thiazolylazo)-resorcin (TAR) wurde erstmalig von Marshall[8] zur photometrischen Bestimmung von Zink benutzt. Evans und Mitarbeiter setzten es zur Zinkbestimmung in Kesselwasser ein.[9] Zwischen Zink-(II)-Ionen und dem Azofarbstoff TAR bildet sich bei pH 7,4–8,4 ein bei 530 nm absorbierender Komplex. Sein Metall–Ligand-Verhältnis wird mit 1:1 angegeben.[10]

Experimenteller Teil

Geräte und Reagentien. Geräte wie bei der Zinkbestimmung mit PAR.

TAR-Lösung: 0,1 %ig in Methanol ($=4{,}1\cdot10^{-3}M$).

Puffer-Lösung: pH 7,5 (15 g Triäthanolamin und 60 ml 1*M* Natriumhydroxid werden mit Wasser auf ein Volumen von 100 ml aufgefüllt, pH 7,5 wird mit 5*M* Saltsäure am pH-Meter eingestellt).

Arbeitsvorschrift. Zu der zinkhaltigen Probelösung (Zn-Gehalt bis 75 µg) gibt man im 50-ml Maßkolben 10 ml Puffer- sowie 1 ml TAR-Lösung und füllt mit Wasser zur Marke auf. Die Messung erfolgt sofort bei 530 nm in 1-cm Küretten gegen eine Reagentienblindlösung.

Ergebnisse

Bemerkungen zum Verfahren. Eine Zusammenstellung der Kennzahlen zur Zinkbestimmung mit TAR enthalten die Tabellen 1–3. Der in der Literatur[8] zur Einhaltung des pH-Wertes vorgegebene Puffer, bestehend aus Triäthanolamin und Natronlauge erwies sich als günstig, da er gleichzeitig als Maskierungsmittel dient.

Nachteilig sind die recht hohen Blindwerte, da das Reagens bei der Meßwellenlänge stark absorbiert. Diese Blindwerte steigen mit zunehmender Alkalinität der Lösung rasch an, so daß der pH-Wert bei der Bestimmung nicht höher als 7,5 sein sollte, obwohl der Zink-TAR-Komplex auch bei höheren pH-Werten noch stabil ist. Bei einer Reagenskonzentration von $8\cdot10^{-5}M$ und pH 7,5 beträgt die Extinktion des Blindwertes 0,825. Ein Erhöhen der Reagensmenge ist also nicht empfehlenswert. Marshall[8] bestimmte Zink aus einer Lösung, die nur $0{,}4\cdot10^{-5}M$ Reagens enthielt. Darin ist sicher auch die Ursache

Tabelle 3. Charakterisierung der Methode (alle Angaben sind auf das Volumen der wäßrigen Phase bezogen)

Name	Arbeitsbereich	Gleichung der Eichgeraden, $\mu g/ml$	Empfindlichkeit, ϵ_λ, $l \cdot mole^{-1} \cdot cm^{-1}$	Reproduzierbarkeit, $\mu g/ml$	Grenzen des Verfahrens, $\mu g/ml$
PAR	0,05–0,9 µg/ml 0,04–0,7 μM	$y = (1{,}318 \pm 0{,}007) \cdot c$	$\epsilon_{495} = 8{,}7 \cdot 10^4$	$s = \pm 0{,}001$ (für 0,4 µg/ml) $v = 0{,}3\%$	0,009
TAR	0,1–1,5 µg/ml 0,08–1,15 μM	$y = (0{,}612 \pm 0{,}010) \cdot c$	$\epsilon_{530} = 4{,}0 \cdot 10^4$	$s = \pm 0{,}005$ (für 0,8 µg/ml) $v = 0{,}6\%$	0,032
PAN	0,05–0,55 µg/ml 0,015–0,168 μM	$y = (0{,}044 \pm 0{,}010) +$ $(1{,}880 \pm 0{,}025) \cdot c$	$\epsilon_{560} = 12{,}4 \cdot 10^4$	$s = \pm 0{,}001$ (für 0,25 µg/ml) $v = 0{,}5\%$	0,033
TAN	0,05–0,7 µg/ml 0,015–0,214 μM	$y = (0{,}148 \pm 0{,}008) \pm$ $(1{,}518 \pm 0{,}009) \cdot c$	$\epsilon_{585} = 10{,}0 \cdot 10^4$	$s = \pm 0{,}006$ (für 0,4 µg/ml) $v = 1{,}1\%$	0,070
Sulfarsazen	0,1–1,6 µg/ml 0,08–1,22 μM	$y = (0{,}705 \pm 0{,}005) \cdot c$	$\epsilon_{505} = 4{,}6 \cdot 10^4$	$s = \pm 0{,}010$ (für 1,0 µg/ml) $v = 1{,}1\%$	0,020
Zincon	0,2–2,6 µg/ml 0,15–2,0 μM	$y = (0{,}365 \pm 0{,}003) \cdot c$	$\epsilon_{625} = 2{,}4 \cdot 10^4$	$s = \pm 0{,}010$ (für 1,2 µg/ml) $v = 0{,}9\%$	0,260
Xylenolorange	0,2–4,0 µg/ml 0,15–3,1 μM	$y = (0{,}369 \pm 0{,}003) \cdot c$	$\epsilon_{575} = 2{,}4 \cdot 10^4$	$s = \pm 0{,}020$ (für 1,2 µg/ml) $v = 1{,}3\%$	0,022
Oxin/Butylamin	0,5–7,0 µg/ml 0,15–2,14 μM	$y = (0{,}013 \pm 0{,}007) +$ $(0{,}147 \pm 0{,}002) \cdot c$	$\epsilon_{400} = 0{,}95 \cdot 10^4$	$s = \pm 0{,}050$ (für 2,5 µg/ml) $v = 0{,}9\%$	0,320
Oxin/$HClO_4$	0,5–4,5 µg/ml 0,15–1,07 μM	$y = (0{,}013 \pm 0{,}011) +$ $(0{,}185 \pm 0{,}004) \cdot c$	$\epsilon_{360} = 1{,}25 \cdot 10^4$	$s = \pm 0{,}100$ µg/ml (für 2,5 µg/ml) $v = 2{,}3\%$	0,070

für den tiefer liegenden Extinktionskoeffizienten zu suchen [$\epsilon_{350} = 3{,}5 \cdot 10^4$ l·mole^{-1}·cm^{-1} (Marshall)[8] und $\epsilon_{350} = 4{,}0 \cdot 10^4$ (eigene Ergebnisse)]. Der p*D*-Wert der Nachweisreaktion von Zink mit TAR beträgt 5,3 bei pH. Eine photometrische Zinkbestimmung mit TAR-Derivaten bringt sowohl bezüglich Empfindlichkeit als auch Selektivität nach Angaben von Adamovich[11] keine Verbesserungen gegenüber TAR (2-Nitro-TAR: $\epsilon_{505} = 3{,}4 \cdot 10^4$ l·mole^{-1}·cm^{-1}; 5-Sulfo-TAR: $\epsilon_{505} = 2{,}4 \cdot 10^4$).

Selektivität des Verfahrens. Unter den angegebenen Bedingungen reagieren folgende Ionen nicht mit dem Reagens und können mindestens bis zum 100-fachen Überschuß (100-fach stellt die Untersuchungsgrenze dar) vorhanden sein: Al(III), As(III), Cr(VI), Fe(III), Ge(IV), Ir(IV), K(I), Mg(II), Na(I), Os(VIII), Pb(II), Pt(IV), Rb(I), Re(VII), Rh(III), Sc(III), Se(IV), Sr(II), Th(IV), Tl(I), V(V), W(VI).

Folgende Ionen stören die Bestimmung entweder durch gleiche Reaktion mit TAR oder durch Ausfallen der Hydroxide:

ab 1:35 Ni(II);
ab 1:25 La(III);
ab 1:20 Ba(II), Pd(II);
ab 1:15 Bi(III), Ce(IV);
ab 1:10 Cu(II), Ga(III), In(III), Mo(VI), Ru(III), Sb(III), Te(VI);
ab 1:5 Mn(II), Nb(V);
ab 1:2 Ag(I), Au(III), Ti(IV), U(VI);
in jedem Verhältnis Be(II), Ca(II), Cd(II), Co(II), Cr(III), Hg(II), Sn(II), Y(III), Zr(IV).

BESTIMMUNG VON ZINK MIT 1-(2-PYRIDYLAZO)-2-NAPHTHOL

Seit Einführung von 1-(2-Pyridylazo)-2-naphthol (PAN) als analytisches Reagens durch Cheng und Bray[12] hat es eine weite Verbreitung zur extraktionsphotometrischen Bestimmung sehr vieler Kationen gefunden.[13]

PAN bildet mit zahlreichen Schwermetallkationen in schwach saurem, neutralem bzw. alkalischem Medium meist rote Komplexe. Püschel[14] beschreibt allgemein die Anwendbarkeit des Reagens in der Spurenanalyse und stellt fest, daß es ein sehr vielseitig anwendbares, dabei aber sehr wenig selektives Reagens ist. Es sind *ca.* 40 Ionen mit hoher Empfindlichkeit bestimmbar.

Berger und Elvers verwendeten PAN als Reagens zur photometrischen Bestimmung von Zink.[15,16] Bei PAN-Überschuß bildet sich ein sehr stabiler 1:2-Komplex, der im pH-Bereich 4,5 bis 10,0 beständig ist.[17] In der Literatur sind eine Reihe von Verfahren zur Bestimmung von Zink in Legierungen und Erzen beschrieben, die der geringen Selektivität des Reagens entweder durch Vorextraktion des Zinks oder durch selektive Maskierung der Störionen begegnen.[18–25]

Halogen- und Nitro-Derivate von PAN wurden ebenfalls zur extraktions-photometrischen Zinkbestimmung eingesetzt. Die Substitution führt zwar zu einer geringen Empfindlichkeitssteigerung, erhöht jedoch die Selektivität nicht wesentlich.[26–28]

Experimenteller Teil

Geräte und Reagentien. Geräte wie bei der Zinkbestimmung mit PAR.

PAN-Lösung: 0,1 %ig in Äthanol ($=4 \cdot 10^{-3} M$).

Puffer-Lösung: pH 6,5 (0,2*M* Natriumacetatlösung wird mit 0,2*M* Essigsäure auf pH 6,5 eingestellt).

Chloroform: p.a.

Arbeitsvorschrift. Zu der zinkhaltigen Probelösung (Zn-Gehalt bis 11 µg) gibt man im Schütteltrichter 5 ml Pufferlösung, ergänzt mit Wasser auf 20 ml und setzt 1 ml PAN-Lösung zu. Zur besseren Durchmischung schüttelt man 30 Sekunden und extrahiert anschließend mit 10,0 ml Chloroform 60 Sekunden. Die organische Phase wird zur Entfernung von Wasserresten über Glaswolle direkt in die Meßküvette filtriert. Die Messung erfolgt sofort bei 560 nm in 1-cm Küvetten gegen Chloroform.

Ergebnisse

Bemerkungen zum Verfahren. Eine Zusammenstellung der Kennzahlen zur Zinkbestimmung mit PAN enthalten die Tabellen 1–3. Abweichend von Literaturangaben[16] fanden wir, daß der Zink–PAN-Komplex am günstigsten im pH-Bereich 6,0 bis 10,0 extrahierbar ist. Aus Selektivitätsgründen wurde bei niedrigem pH-Wert (6,5) gearbeitet. In diesem Bereich liegt der Blindwert mit einer Extinktion von 0,05 recht günstig.

Die in der Literatur angegebenen Extinktionskoeffizienten (bezogen auf das Volumen der organischen Phase unter der Voraussetzung der vollständigen Extraktion) konnten bestätigt werden: $\epsilon_{560} = 5{,}6 \cdot 10^4$ l·mole^{-1}·cm^{-1} (Berger und Elvers)[14]; $5{,}8 \cdot 10^4$ (Flaschka und Weiss)[24] und $6{,}2 \cdot 10^4$ (eigene Ergebnisse).

Der p*D*-Wert der Nachweisreaktion von Zink mit PAN beträgt 5,7 bei pH 7.

Selektivität des Verfahrens. Unter den angegebenen Bedingungen reagieren folgende Ionen nicht mit dem Reagens und können mindestens bis zum 100-fachen Überschuß (100-fach stellt die Untersuchungsgrenze dar) vorhanden sein: Ag(I), Al(III), As(III), Au(III), Ba(II), Be(II), Ca(II), Ce(IV), Cr(III, VI), Ga(III), In(III), K(I), La(III), Li(I), Mg(II), Mo(VI), Na(I), Nb(V), Os(VIII), Pb(II), Pt(IV), Rb(I), Re(VII), Rh(III), Ru(III), Sb(III), Sc(III), Se(IV), Sr(II), Te(VI), Th(IV), Ti(IV), Tl(I), W(VI), Y(III), Zr(IV).

Folgende Ionen stören die Bestimmung durch gleiche Reaktion mit PAN:

ab 1:20 Bi(III), Ge(IV), Pd(II);
ab 1:10 Ir(IV);
in jedem Verhältnis Cd(II), Co(II), Cu(II), Fe(II, III), Hg(II), Mn(II), Ni(II), Sn(II), U(VI), V(V).

BESTIMMUNG VON ZINK MIT 1-(2-THIAZOLYLAZO)-2-NAPHTHOL

Boni und Hemmeler[29] verwendeten 1-(2-Thiazolylazo)-2-naphthol (TAN) erstmalig zum Nachweis von Schwermetallkationen, besonders von Kupfer, Kobalt

und Zink, im alkalischen Medium. Als photometrisches Reagens zur Bestimmung von Zink wurde TAN von Kawase[30] vorgeschlagen.

Die Extraktion des rotvioletten wasserunlöslichen Zink–TAN-Komplexes erfolgt am günstigsten bei pH 8 mit Chloroform. Nach Literaturangaben soll mit TAN gegenüber PAN eine Selektivitätssteigerung erreicht werden.[30] Wir konnten diese Angaben nicht bestätigen. Die Komplexbildung von Zinkionen mit TAN erfolgt stufenweise. In schwach alkalischem Medium und bei Reagensüberschuß liegt ein 1:2-Komplex vor.[17]

Experimenteller Teil

Geräte und Reagentien. Geräte wie bei der Zinkbestimmung mit PAR.

TAN-Lösung: 0,025 %ig in Methanol ($=10^{-3}M$).

Puffer-Lösung: pH 7,0 (0,2*M* Natriumacetatlösung wird mit 0,2*M* Essigsäure auf pH 7,0 eingestellt).

Chloroform p.a.

Arbeitsvorschrift. Zu der zinkhaltigen Probelösung (Zink-Gehalt bis 14 μg) gibt man im Schütteltrichter 10 ml Puffer- sowie 3 ml TAN-Lösung, füllt mit Wasser zu einem Volumen von *ca.* 20 ml auf und läßt die Mischung 5 min stehen. Anschließend extrahiert man mit 10,0 ml Chloroform 60 Sekunden. Die organische Phase wird zur Entfernung von Wasserspuren zentrifugiert und bei 585 nm in 1-cm Küvetten sofort gegen Chloroform gemessen.

Ergebnisse

Bemerkungen zum Verfahren. Eine Zusammenstellung der Kennzahlen zur Zinkbestimmung mit TAN enthalten die Tabellen 1–3. Der von Kawase[30] angewandte Puffer zur Einstellung des pH-Wertes auf 8,5, der aus einer Mischung von Acetat- und Boratpuffer besteht, erwies sich als wenig geeignet. Die Meßergebnisse waren schlecht reproduzierbar. Nach unseren Untersuchungen ist die Extraktion aus einer Lösung von pH 7,0–7,5, eingestellt mit Acetatpuffer, optimal. Die Reagenskonzentration wurde gegenüber der Arbeitsvorschrift der Literatur verdreifacht, was bei noch vertretbarem Blindwert ($E = 0{,}15$) eine Erweiterung des Arbeitsbereiches zur Folge hat (Arbeitsbereich nach[30] 0,03–0,8 μg Zn/ml $CHCl_3$, eigene Ergebnisse 0,1–1,4 μg/ml). Der in der Literatur angegebene Extinktionskoeffizient (bezogen auf das Volumen der organischen Phase unter der Voraussetzung der vollständigen Extraktion) von $\epsilon_{580} = 5{,}0 \cdot 10^4$ $l \cdot mole^{-1} \cdot cm^{-1}$ konnte bestätigt werden.

Der p*D*-Wert der Nachweisreaktion von Zink mit TAN beträgt 5,5 bei pH 7.

Selektivität des Verfahrens. Unter den angegebenen Bedingungen reagieren folgende Ionen nicht mit dem Reagens und können mindestens bis zum 100-fachen Überschuß (100-fach stellt die Untersuchungsgrenze dar) vorhanden sein: As(III), Ba(II), Bi(III), Ca(II), Cr(III, VI), K(I), La(III), Li(I), Mg(II), Mo(VI), Na(I), Rb(I), Re(VII), Sc(III), Se(IV), Sr(II), Tl(I), V(V), W(VI).

Folgende Ionen stören die Bestimmung entweder durch gleiche Reaktion mit TAN oder durch Ausfallen der Hydroxide:

ab 1:50 Ge(IV), Te(VI);
ab 1:25 Ce(IV), Pb(II), Pt(IV);
ab 1:10 Ga(III), Th(IV), Zr(IV);
ab 1:5 Rh(III);
ab 1:2 Ag(I), Ir(IV), Sn(II), Ti(IV);
in jedem Verhältnis Al(III), Be(II), Cd(II), Co(II), Cu(II), Fe(II, III), Hg(II), In(III), Mn(II), Ni(II), Pd(II), Ru(III), U(VI).

BESTIMMUNG VON ZINK MIT SULFARSAZEN

In alkalischem Medium (pH 8,0–9,8) bildet Sulfarsazen (4-Nitro-2-arsonobenzol-1,4′-diazoamino-1′,1″-azobenzol-4″-sulfonsäure, Natrium-Salz) mit den Ionen Ag(I), Cd(II), Cu(II), Hg(II), Mn(II), Ni(II), Pb(II) und Zn(II) farbige Komplexe, die zur photometrischem Bestimmung der genannten Elemente geeignet sind.[31,32] Nach Angaben von Partashnikova[33] bildet Zink mit Sulfarsazen einen bei 500 nm absorbierenden 1:1-Komplex.

Experimenteller Teil

Geräte wie bei der Zinkbestimmung mit PAR.

Sulfarsazenlösung: 0,005 %ig in 0,05*M* Natriumtetraboratlösung ($=8{,}7 \cdot 10^{-4}M$).

Puffer-Lösung: pH 9,5 (0,1*N* Natriumtetraboratlösung wird mit 0,1*N* Salzsäure auf pH 9,5 eingestellt).

Arbeitsvorschrift. Zu der zinkhaltigen Probelösung (Zn-Gehalt bis 80 μg) gibt man im 50-ml Maßkolben 5 ml Puffer- sowie 4 ml Sulfarsazenlösung und füllt mit Wasser zur Marke auf. Die Messung erfolgt sofort bei 505 nm in 1-cm Küvetten gegen Reagentienblindlösung.

Ergebnisse

Bemerkungen zum Verfahren. Eine Zusammenstellung der Kennzahlen zur Zinkbestimmung mit Sulfarsazen enthalten die Tabellen 1–3. In der Literatur wird die Bestimmung von Zink bei pH 9,3–9,6 unter Verwendung von Ammoniak–Ammoniumchlorid-Puffer beschrieben.[31] Eigene Untersuchungen ergaben jedoch, daß sich ab pH 7,0 Zink–Ammin-Komplexe bilden, die stabiler als der Zink–Sulfarsazen-Komplex sind. Wir verwendeten deshalb zur Einstellung des pH-Wertes einen Boratpuffer. Da die Komplexbildung stark von der Ionenstärke der Lösung abhängig ist, muß die Puffermenge so bemessen werden, daß $I \leqslant 0{,}05$.

Der ermittelte Extinktionskoeffizient stimmt mit den Angaben von Petrova[31] überein [$\epsilon_{505} = 4{,}6 \cdot 10^4$ $l \cdot mole^{-1} \cdot cm^{-1}$ und $\epsilon_{500} = 4{,}5 \cdot 10^4$ (eigene Ergebnisse)].

Der p*D*-Wert der Nachweisreaktion von Zink mit Sulfarsazen beträgt 5,3 bei pH 9.

Das Reagens wurde auch zur Bestimmung von Zink in Legierungen und Erzen verwendet.[34,35]

Selektivität des Verfahrens. Unter den angegebenen Bedingungen reagieren folgende Ionen nicht mit dem Reagens und können mindestens bis zum 100-fachen Überschuß (100-fach stellt die Untersuchungsgrenze dar) vorhanden sein: As(III), Ga(III), Ge(IV), Ir(IV), K(I), Li(I), Mo(VI), Na(I), Os(VIII), Pd(II), Rb(I), Re(VII), Sb(V), Se(IV), Te(VI), Tl(I), V(V), W(VI).

Folgende Ionen stören die Bestimmung entweder durch gleiche Reaktion mit Sulfarsazen oder durch Ausfallen der Hydroxide:

ab 1:20 Au(III), Cr(VI);
ab 1:15 La(III);
ab 1:10 Mg(II);
ab 1:5 Bi(III), Sr(II);
ab 1:2 Ba(II), Ca(II), Th(IV);
in jedem Verhältnis Ag(I), Al(III), Cd(II), Ce(IV), Co(II), Cr(III), Cu(II), Fe(II, III), Hg(II), In(III), Mn(II), Ni(II), Pb(II), Sc(III), Sn(II), U(VI), Zr(IV).

BESTIMMUNG VON ZINK MIT ZINCON

Zincon (2-Carboxy-2'-hydroxy-5'-sulfoformazylbenzol) bildet mit einigen Metallionen [wie z.B. Cu(II), Co(II), Ni(II), Zn(II)] in alkalischem Medium intensiv blaue Komplexe. Rush und Yoe[36,37] beschreiben die photometrische Bestimmung von Kupfer und Zink nebeneinander mit Zincon. Das gleiche Reagens wurde auch zur photometrischen Bestimmung von Zink in Düngesalzen und anderen Matrizes herangezogen.[38–40]

Der sich bei pH 8 bildende Zink–Zincon-Komplex hat die Zusammensetzung Me:R = 1:1.[41]

Experimenteller Teil

Geräte und Reagentien. Geräte wie bei der Zinkbestimmung mit PAR.

Zincon-Lösung: 0,13 %ig in Äthanol ($=3\cdot10^{-3}M$).

Puffer-Lösung: pH 9,0 (0,1*N* Natriumtetraboratlösung wird mittels 0,1*M* Salzsäure auf pH 9,0 eingestellt).

Arbeitsvorschrift. Zu der zinkhaltigen Probelösung (Zn-Gehalt bis 130 µg) gibt man im 50-ml Maßkolben 30 ml Puffer- sowie 4 ml Zinconlösung und füllt mit Wasser zur Marke auf. Die Messung erfolgt sofort bei 625 nm in 1-cm Küvetten gegen eine Reagentienblindlösung.

Ergebnisse

Bemerkungen zum Verfahren. Eine Zusammenstellung der Kennzahlen zur Zinkbestimmung mit Zincon enthalten die Tabellen 1–3. Die in der Literatur[36] verwendete alkalische Reagenslösung (Zincon in 0,02*N* Natronlauge bzw. Ammoniak) erwies sich nach unseren Untersuchungen als ungeeignet, da diese Lösung schon innerhalb 24 Stunden große Veränderungen in der Extinktion zeigte. Wir verwendeten mit Erfolg eine äthanolische Lösung, die 3 Wochen stabil war.

Die berechnete Empfindlichkeit des Verfahrens stimmt mit den Literaturdaten überein ($\epsilon_{625} = 2{,}2\cdot10^4\,l\cdot mole^{-1}\cdot cm^{-1}$ (Rush und Yoe)[36] und $2{,}4\cdot10^4$ (eigene Ergebnisse)].

Der p*D*-Wert der Nachweisreaktion von Zink mit Zincon beträgt[5,2] bei pH 9.

Selektivität. Unter den angegebenen Bedingungen reagieren folgende Ionen nicht mit dem Reagens und können mindestens bis zum 100-fachen Überschuß (100-fach stellt die Untersuchungsgrenze dar) vorhanden sein: As(III), Ba(II), Ca(II), Cr(VI), Ge(IV), K(I), Li(I), Mg(II), Mo(VI), Na(I), Nb(V), Pt(IV), Rb(I), Re(VII), Sb(III), Se(IV), Sr(II), Te(VI), Tl(I), U(VI), V(V), W(VI).

Folgende Ionen stören die Bestimmung entweder durch gleiche Reaktion mit Zincon oder durch Ausfallen der Hydroxide:

ab 1:25 IR(IV);
ab 1:15 Au(III), Pb(II), Y(III);
ab 1:5 Ce(IV), Ga(III);
ab 1:2 La(III), Pd(II);
in jedem Verhältnis Ag(I), Al(III), Be(II), Bi(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(II, III), Hg(II), In(III), Mn(II), Ni(II), Rh(III), Ru(III), Sc(III), Sn(II), Th(IV), Ti(IV), Zr(IV).

BESTIMMUNG VON ZINK MIT XYLENOLORANGE

Študlar und Janoušek[42] bestimmten Zink photometrisch mit Xylenolorange als Reagens. Demnach bildet sich im pH-Bereich 5,8–6,2 ein roter 1:1-Komplex. Das Reagens ist wie auch alle anderen Sulfophthaleinfarbstoffe sehr wenig selektiv, so daß eine vorangehende Abtrennung des Zinks unbedingt nötig ist.

Die Bildung eines 1:1-Chelates wurde auch von Bulatov[43] bestätigt. Abweichend davon bewiesen Mukrami und Mitarbeiter,[44] daß Xylenolorange einen 1:2-Komplex mit Zink bildet, während das durch Semixylenolorange und andere Verbindungen verunreinigte Handelsprodukt im Verhältnis 1:1 reagiert. Sicher ist, daß das Handels-Xylenolorange neben Semixylenolorange die Ausgangsprodukte der Synthese *o*-Kresolrot und Iminodiessigsäure enthält, so daß komplexchemische Daten, die mit diesem Reagens erhalten wurden, nicht immer exakt sein müssen.[45] Für die ermittelten Kennzahlen gilt diese Einschränkung natürlich auch.

Andere, in der Komplexometrie als Indikatoren für Schwermetallionen verwendete Sulfophthaleinfarbstoffe, wie z.B. Methylthymolblau, Glycinthymolblau, Glycinkresolrot und Bromkresolorange sind ebenfalls als Reagentien zur photometrischen Zinkbestimmung geeignet. Die damit erzielten Empfindlichkeiten liegen unter der bei der Bestimmung mit Xylenolorange und auch bezüglich Selektivität sind diese Farbstoffe Xylenoloroange unterlegen.

Experimenteller Teil

Geräte und Reagentien. Geräte wie bei der Zinkbestimmung mit PAR.

Xylenolorange-Lösung: $10^{-3}M$ in 10 %igem Äthanol.

Puffer-Lösung: pH 6,0 (0,2*M* Natriumacetatlösung wird mit 0,2*M* Essigsäure auf pH 6,0 eingestellt).

Arbeitsvorschrift. Zu der zinkhaltigen Probelösung (Zn-Gehalt bis 200 µg) gibt man im 50-ml Maßkolben 5 ml Puffer- sowie 5 ml Xylenolorangelösung und füllt mit Wasser zur Marke auf. Die Messung erfolgt sofort bei 575 nm in 1-cm Küvetten gegen Reagentienblindlösung.

Ergebnisse

Bemerkungen zum Verfahren. Eine Zusammenstellung der Kennzahlen zur Zinkbestimmung mit Xylenolorange enthalten die Tabellen 1–3. Die Bil-

dung des roten Zink–Xylenolorange-Chelates beginnt bei pH 4,0 und ist optimal zwischen pH 5,5 und 6,0. Bei diesem pH-Wert besitzt das Reagens selbst schon ein ausgeprägtes Maximum am Absorptionsmaximum des Komplexes (575 nm). Diese Tatsache ist aus der Literatur bekannt[42] und konnte von uns bestätigt werden. Wir fanden bei unseren Untersuchungen, daß die Menge der Pufferlösung einen Einfluß auf die Extinktion hat, da die Komplexbildung stark von der Ionenstärke der Lösung abhängig ist. Ein Anwachsen der Ionenstärke von $I = 0{,}02$ (=5 ml Pufferlösung) auf $I = 0{,}1$ (=25 ml Pufferlösung) führt zu einer Empfindlichkeitsabnahme von 10 %.

Die zeitliche Stabilität des Zink–Xylenolorange-Komplexes ist bis zu 45 Minuten gegeben, währenddessen Študlar 3-Stunden Konstanz der Meßwerte angibt.[42]

Die erzielten Extinktionskoeffizienten sind mit den Werten der Literatur nur zum Teil übereinstimmend: $\epsilon_{575} = 2{,}75 \cdot 10^4$ $l \cdot mole^{-1} \cdot cm^{-1}$, (Bagdarasov und Mitarbeiter),[46] $1{,}2 \cdot 10^4$ (Gurkina und Igoshim)[47] und $2{,}4 \cdot 10^4$ (eigene Untersuchungen).

Der p*D*-Wert der Nachweisreaktion von Zink mit Xylenolorange beträgt 4,7 bei pH 5.

Wie es zu erwarten war, erwies sich Xylenolorange als sehr wenig selektives Zinkreagens. Umfassende Untersuchungen sind aus der Literatur hierzu nicht bekannt.

Selektivität des Verfahrens. Unter den angegebenen Bedingungen reagieren folgende Ionen nicht mit dem Reagens und können mindestens bis zum 100-fachen Überschuß (100-fach stellt die Untersuchungsgrenze dar) vorhanden sein: Ag(I), AS(III), Ba(II), Cr(III, VI), K(I), Li(I), Mo(VI), Na(I), Nb(V), Os(VIII), Pt(IV), Rb(I), Re(VII), Rh(III), Ru(III), Se(IV), Sr(II), Tl(I), W(VI).

Folgende Ionen stören die Bestimmung entweder durch gleiche Reaktion mit Xylenolorange oder durch Ausfallen der Hydroxide:

ab 1:20 Au(III), In(III), Pd(II), U(VI), Zr(IV);
ab 1:10 Bi(III), Ge(IV), Ir(IV), Mg(II), Sb(III), Te(VI), Ti(IV);
ab 1:2 Ca(II), Fe(II, III), Ga(III), Sn(II), V(V);
in jedem Verhältnis Al(III), Be(II), Ce(III, IV), Cd(II), Co(II), Cu(II), Hg(II), La(III), Mn(II), Ni(II), Pb(11), Sc(III), Th(IV), Y(III).

BESTIMMUNG VON ZINK MIT 8-HYDROXYCHINOLIN UND N-BUTYLAMIN

Extrahiert man Zink(II)-Ionen aus wäßriger Lösung mit oxinhaltigem Chloroform, so werden binäre Komplexe der Zusammensetzung $ZnOx_2$ (Ox = 8-Hydroxychinolin) gebildet. Diese tetraedrische Koordination ist instabil und geht nach Umland und Hoffmann[48] unter Aufnahme von 2 Wassermolekülen in eine Oktaederform $ZnOx_2 \cdot 2H_2O$ über. Die Löslichkeit dieser Komplexe in organischen Solventien ist gering, d.h. die Extraktion wird wenig reproduzierbar und nicht quantitativ. Wird die Extraktion in Gegenwart von primärem oder sekundärem Butylamin durchgeführt, so entsteht ein Komplex der Zusammensetzung $ZnOx_2 \cdot C_4H_9NH_2 \cdot H_2O$ ($C_4H_9NH_2$ = n-Butylamin). Dieser ist genügend stabil und gut chloroformlöslich.[48]

Experimenteller Teil

Geräte und Reagentien. Geräte wie bei der Zinkbestimmung mit PAR.

8-Hydroxychinolin-Lösung: $10^{-3}M$ in Chloroform.

n-Butylamin p.a.

Arbeitsvorschrift. Zu der neutralen zinkhaltigen Probelösung (Zn-Gebalt bis 100 μg) gibt man im Schütteltrichter 0,2 ml n-Butylamin und bringt das Gesamtvolumen der Lösung auf *ca.* 20 ml. Nach Zugabe von 10,0 ml 8-Hydroxychinolin–Chloroform-Lösung schüttelt man 60 Sekunden. Sind die Phasen klar (nach 5 Minuten), trennt man die organische Schicht ab und bestimmt deren Extinktion nach einer Wartezeit von 10 Minuten bei 400 nm in 1-cm Küvetten gegen Chloroform.

Ergebnisse

Bemerkungen zum Verfahren. Eine Zusammenstellung der Kennzahlen zur Zinkbestimmung mit 8-Hydroxychinolin/n-Butylamin enthalten die Tabellen 1–3. Bei niedrigen pH-Werten (<8,5) liegt das Absorptionsmaximum der extrahierten Verbindung bei 380 nm. Dieses Maximum ist dem binären Komplex $ZnOx_2$ zuzuordnen. Der aminhaltige Komplex wird erst bei pH-Werten oberhalb pH 8,5 extrahiert; er besitzt bei 400 nm ein Absorptionsmaximum. Der für die Extraktion optimale pH-Wert liegt im Bereich von pH 10–12. Die Basizität und die Pufferwirkung des Amins sind in der Lage, einen konstanten pH-Wert von 11 zu gewährleisten, so daß auf Anwendung eines Puffers verzichtet werden kann.

Meßtechnisch günstig ist, daß der Komplex über einen längeren Zeitraum (d.h. mehrere Stunden) stabil ist.

Die Konzentration an Amin wurde gegenüber der Vorschrift aus der Literatur erhöht (von 0,08 auf 2% bezogen auf das Volumen der organischen Phase). Wir fanden, daß zu geringe Amingehalte zu instabilen Lösungen führen, die nach Umland und Hoffmann mit Methanol stabilisiert werden müssen,[48] was bei unserer Verfahrensweise nicht nötig ist. Der in der Literatur angegebene molare Extinktionskoeffizient von $5{,}95 \cdot 10^3$ $l \cdot mole^{-1} \cdot cm^{-1}$ konnte nicht erreicht werden. [$\epsilon_{400} = 4{,}75 \cdot 10^3$ (eigene Ergebnisse)].

Selektivität des Verfahrens. Unter den angegebenen Bedingungen reagieren folgende Ionen nicht mit dem Reagens und können mindestens bis zum 100-fachen Überschuß (100-fach ist die Untersuchungsgrenze) vorhanden sein: As(III), Ba(II), Ca(II), Cr(VI), Cs(I), Ge(IV), K(I), Li(I), Na(I), Nb(V), Pt(IV), Rb(I), Re(VII), Se(IV), Sr(II), Ta(V), Te(VI), Th(IV), Tl(I), W(VI).

Folgende Ionen stören die Bestimmung entweder durch gleiche Reaktion mit 8-Hydroxychinolin oder durch Ausfallen der Hydroxide:

ab 1:20 Al(III), Ir(IV), Sb(V), Y(III);
ab 1:5 Au(III), La(III), Mo(VI), Sn(II), V(V);

in jedem Verhältnis Ag(I), Be(II), Bi(III), Cd(II), Ce(IV), Co(II), Cr(III), Cu(II), Fe(III), Ga(III), Hg(II), In(III), Mg(II), Mn(II), Ni(II), Pb(II), Pd(II), Rh(III), Ru(III), Sc(III), Ti(IV), U(VI), Zr(IV).

BESTIMMUNG VON ZINK MIT 8-HYDROXYCHINOLIN UND PERCHLORAT

Zink(II)-Ionen werden in schwach saurem Medium in Gegenwart von 8-Hydroxychinolin in ein komplexes hydrophobes Kation überführt, das mit dem Perchloratanion ein mit Chloroform extrahierbares Ionenpaar bildet. Oki und Tereda[49] extrahierten auf diese Weise Zink quantitativ im pH-Bereich 4–6. In der organischen Phase liegt nach ihren Angaben[50] die folgende Verbindung vor: $[Zn_2(Ox)_3(HOx)_3^+, ClO_4^-]$. In Abhängigkeit von der angewandten Reagensmenge können aber auch anders zusammengesetzte Komplexe entstehen: $[Zn(HOx)^{2+}, Ox^- ClO_4^-]$, $[Zn(HOx)^{2+}, 2ClO_4^-]$ oder $[Zn(HOx)_3^{2+}, Ox^- \cdot ClO_4^-]$.

Experimenteller Teil

Geräte und Reagentien. Geräte wie bei der Zinkbestimmung mit PAR.

8-Hydroxychinolinlösung: $1{,}5 \cdot 10^{-2} M$ in Dichloräthan.

Perchlorsäurelösung: 0,4*M*.

Puffer-Lösung: pH 5,7 (hergestellt aus Natriumacetatlösung und Essigsäure, die Ionenstärke des Puffers soll *ca.* 1,0 sein).

Arbeitsvorschrift. Zu der zinkhaltigen Probelösung (Zn-Gehalt bis 90 µg) gibt man im Schütteltrichter 5 ml Puffer-, 5 ml Perchlorat- sowie 10,0 ml 8-Hydroxychinolinlösung und extrahiert 2 Minuten. Die Extinktion des abgetrennten Dichloräthanextraktes wird sofort bei 365 nm in 1-cm Küvetten gegen Blindextrakt gemessen.

Ergebnisse

Bemerkungen zum Verfahren. Eine Zusammenstellung der Kennzahlen zur Zinkbestimmung mit 8-Hydroxychinolin/Perchlorat enthalten die Tabellen 1–3. Das Absorptionsmaximum des Ionenpaares liegt bei 360 nm und damit im Absorptionsbereich des Blindwertes. Die Messungen wurden deshalb nicht am Absorptionsmaximum, sondern bei 365 nm ausgeführt, wo der Blindextrakt eine zwar hohe, aber meßbare Extinktion besitzt.

Der optimale pH-Bereich befindet sich zwischen pH 4,5 und 5,5, d.h. das Gebiet ist etwas schmaler als das in der Literatur angegebene.[49]

Extraktionsversuche ergaben, daß n-Butanol oder Dichloräthan zur Extraktion des Ionenpaares besser geeignet sind als Chloroform. Da die zeitliche Stabilität des Komplexes in Dichloräthan bedeutend höher ist als in n-Butanol (hier beginnt die Zersetzung bereits nach 10 Minuten) wurde dem Dichloräthan als Extraktionsmittel der Vorzug gegeben.

Die Extraktion des Komplexes ist von der Ionenstärke der Lösung abhängig. Sie erreicht bei einer Ionenstärke von >0,8 konstante Werte. Sehr hohe Ionenstärken sind allerdings unvorteilhaft (>1,2), da sie die Phasentrennung im negativen Sinne beeinflussen.

Das Verfahren ist ebenso wie das der Extraktion als Neutralchelat sehr wenig selektiv. Die von uns ermittelten Störionen stimmen mit den Literaturangaben überein.[50]

Selektivität des Verfahrens. Unter den angegebenen Bedingungen reagieren folgende Ionen nicht mit dem Reagens bzw. die Reaktionsprodukte sind nicht extrahierbar und können mindestens bis zum 100-fachen Überschuß (100-fach ist die Untersuchungsgrenze) vorhanden sein: As(III), Ba(II), Ca(II), Cr(III, VI), Cs(I), K(I), La(III), Li(I), Na(I), Nb(V), Pt(IV), Rb(I), Re(VII), Se(IV), Sr(II), Ta(V), Te(VI), Tl(I), Y(III).

Folgende Ionen stören die Bestimmung entweder durch gleiche Reaktion mit 8-Hydroxychinolin oder durch Ausfallen der Hydroxide:

ab 1:20 Ag(I), Mg(II), Rh(III), Ru(III);
ab 1:10 Be(II), Ge(IV), Ir(IV);
ab 1:5 Mn(II), Pb(II);
in jedem Verhältnis Al(III), Bi(III), Cd(II), Ce(IV), Co(II), Cu(II), Fe(III), Ga(III), Hg(II), In(III), Mo(VI), Ni(II), Pd(II), Sb(V), Sn(II), Th(IV), Ti(IV), U(VI), V(V), W(VI), Zr(IV).

SCHLUßFOLGERUNGEN

Wie schon aus der Literatur bekannt ist, haben sämtliche Reagentien, die zur photometrischen Bestimmung von Zink geeignet sind, den Nachteil der sehr geringen Selektivität. Die Anwendung von Maskierungsreagentien oder von geeigneten Trennverfahren, wie Ionenaustausch und Extraktion, sind also unbedingt erforderlich. Dieses sollte aber nicht Gegenstand unserer Untersuchungen sein. Empfehlenswert für eine photometrische Zinkbestimmung sind nach unseren Ergebnissen (siehe Tabelle 1–3) wegen der hohen Empfindlichkeit sowie der guten Reproduzierbarkeit die Verfahren mit den Azofarbstoffen 4-(2-Pyridylazo)-resorcin, 4-(2-Thiazolylazo)-resorcin bzw. 1-(2-Pyridylazo)-naphthol als Reagentien.

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Summary—A systematic investigation scheme was used to examine and evaluate critically the established methods for spectrophotometric determination of zinc with the reagents 4-(2-pyridylazo)resorcinol, 4-(2-thiazolylazo)resorcinol, 1-(2-pyridylazo)-2-naphthol, 1-(2-thiazolylazo)-2-naphthol, Sulpharsazen, Zincon, Xylenol Orange and 8-hydroxyquinoline.

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DETERMINATION OF SMALL AMOUNTS OF BORON BY RADIATION DECOMPOSITION OF CHLOROACETIC ACID SOLUTION*

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Summary—For the determination of boron in the μg/g range in aqueous solution by activation analysis an indirect method is proposed, based on the liberation of chloride ions from chloroacetic acid by the primary reaction $^{10}B(n, \alpha)^{7}Li$. The sample solution, to which is added 0.01–0.5*M* choroacetic acid, is irradiated with reactor neutrons. The concentration of the chloride ions liberated from the chloroacetic acid is directly proportional to the boron content of the irradiated sample. It is determined potentiometrically with a chloride-sensitive electrode. By this method boron contents $\geq 10^{-5}$ g can be detected with good reproducibility. Interference from other ionic species has been investigated and can be neglected. The method is suitable for the determination of boron in biological matrices.

Many chemical methods, with various sensitivities, have been reported for the determination of boron. These are based on spectrophotometric,[1–4] fluorimetric,[5,6] atomic absorption[7–9] and emission[10–12] spectrometric techniques. Owing to the non-availability of suitable radionuclides of boron, nuclear techniques have seldom been used for the determination of boron. A radio-reagent method based on the reaction of boric acid with hydrofluoric acid labelled with fluorine-18 was, however, reported to be suitable for the determination of boron in the submicrogram range.[13]

The present study was initiated to develop a new method for the indirect determination of boron based on the measurement of a specific product of the radiation decomposition of a chemical system. The principle of this method lies in the fact that when a sample containing boron and chloroacetic acid is subjected to neutron irradiation, the charged particles (^{7}Li and ^{4}He) resulting from the nuclear reaction $^{10}B(n, ^{4}He)^{7}Li$, will immediately interact with chloroacetic acid, forming radiation decomposition products such as chloride. It is well known that the concomitant radiation (fast neutrons and γ-rays) arising during reactor neutron irradiation can also lead to such reaction products. The radiation decomposition process can be expressed as

$$CH_2ClCOOH \xrightarrow[(n,\gamma)]{^{4}He,\ ^{7}Li} Cl^- + \text{other radiolytic fragments.}$$

By measurement of the halide ions produced, with a chloride-sensitive electrode, the boron content in the sample can be deduced from the relationship between the boron concentration and the halide concentration induced by fission radiation. It is of primary importance that the effect of the concomitant radiation on the formation of chloride ions during neutron irradiation should be taken into account. Other factors which influence the usefulness and applicability of this method to the determination of small amounts of boron must also be investigated.

EXPERIMENTAL

Reagents and apparatus

All chemicals used in this study were of analytical-reagent grade. An Ionanalyzer Chloride Electrode Model 94–17 coupled with an Orion Model 701 Specific Ion Meter (Orion Research Inc.) was used to measure chloride ion concentrations.

Pretreatment of sample for analysis

A pretreatment which includes separation and enrichment steps is needed in the method. Various interfering ions which might influence the result of the analysis should be removed prior to the determination. Halide ions are

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eliminated by adding concentrated nitric acid to the sample and evaporating to dryness. The metal ions (Hg^{2+}, Ag^{+}, Cu^{2+}, *etc.*) which form complexes with chloride are extracted with sodium diethyldithiocarbamate in chloroform before adjustment of the pH to 2–3. The aqueous phase is then evaporated to dryness after addition of nitric acid.

Another method of separation and enrichment is to distil the boron as methyl borate, which is absorbed in a mixture of glycerol and aqueous alkali.[14]

Preparation of solution for irradiation

The pretreated samples were dissolved along with enough chloroacetic acid to produce a final concentration between 0.01 and 0.3*M*. Five ml of this solution were sealed in a quartz tube (5 cm × 2 cm diameter) for irradiation.

Neutron irradiation

Sample solutions were irradiated with thermal neutrons in the THOR reactor of National Tsing Hua University for times ranging from 10 sec to 2 min. The thermal-neutron flux at the irradiation position was about 2.1×10^{12} $n.cm^{-2}.sec^{-1}$ and the ionizing radiation was estimated to be about 4.5×10^{3} rad/sec. The irradiation temperature was about 30°.

Measurement of chloride

After irradiation the sample was cooled for 1 hr to allow for the decay of short-lived nuclides. The concentration of chloride ions produced was then measured with a chloride-sensitive electrode.

Analysis of samples

Attempts were made to determine the boron content in water and biological samples. For the analysis of boron-contaminated waste-water, a 100-ml water sample was taken and its pH adjusted to 2–3 with nitric acid. It was then extracted with 0.1*M* sodium diethyldithiocarbamate in chloroform. The aqueous phase was added to nitric acid and slowly evaporated to dryness. The residue was dissolved in 0.2*M* chloroacetic acid to give a final volume of 5 ml for neutron irradiation. The loss of boron for the whole process was shown to be negligible by an atomic-absorption spectrometric analysis.

As a model for the analysis of biological material, a sample of orchard leaves (NBS SRM 1571) was digested in a mixture of nitric acid and hydrogen peroxide and evaporated to a small volume to expel excess of water. After addition of methanol and concentrated sulphuric acid, the solution was heated to 80° to distil the methyl borate, which was carried in a nitrogen stream to the collecting solution containing glycerine and 1% sodium hydroxide. The solution was treated further by evaporation and addition of chloroacetic acid for subsequent neutron irradiation.

RESULTS AND DISCUSSION

In the determination of boron by the radiation-induced decomposition of chloroacetic acid, two sources of radiation are responsible for the formation of chloride ions. One consists of the high-energy charged particles resulting from the fission reaction $^{10}B(n, {}^{4}He)^{7}Li$, while the other is the concomitant radiation (fast neutrons and γ-rays) accompanying thermal neutrons in the nuclear reactor. Each type of radiation has a different efficiency in the radiolysis of chloroacetic acid and a quantitative assessment of the relative doses of the two radiations is required to establish the feasibility and limits of detection of the method.

An estimation of the fission radiation dose from the nuclear reaction $^{10}B(n, {}^{4}He)^{7}Li$ can be made from the following data: ^{10}B abundance 18.7%, fission cross-section 3990 barn, fission energy 2.973 MeV. If the thermal-neutron flux is taken as 2.1×10^{12} $n.cm^{-2}.sec^{-1}$ (corresponding to the flux at the irradiation position of the THOR reactor) and the boron content in the sample solution as 0.01%, the total fission radiation dose is calculated to be 4.2×10^{3} rad/sec. The reactor radiation dose at a fixed irradiation position in a reactor can be determined experimentally.[15] The radiation dose in THOR was determined to be 1.9×10^{7} rad/hr for γ-rays and 6.7×10^{6} rad/hr for fast neutrons. The radiation doses for samples with various boron contents are given in Table 1. It is seen that the fission radiation dose decreases with decreasing boron concentration, in contrast to the constant reactor radiation dose under the fixed irradiation condition. As the concentration of boron decreases to 0.01%, the two radiation doses attain nearly equal levels. Obviously the halide ions estimated at lower boron concentrations (<0.001%) are due predominantly to the effect of reactor radiation rather than to that of fission radiation. The limit of detection for boron can be estimated to be around 10 ppm under the present experimental conditions.

The measured chloride concentration for chloroacetic acid solutions containing boron will contain contributions resulting from both fission radiation and reactor radiation. The chloride concentration due solely to the effect of fission radiation by $^{10}B(n,$

Table 1. Comparison of the radiation dose rate for samples with various boron contents

B concentration, %	Fission radiation dose, *rad/sec*	Reactor radiation dose, *rad/sec*
1	4.2×10^{5}	4.5×10^{3}
0.1	4.2×10^{4}	4.5×10^{3}
0.01	4.2×10^{3}	4.5×10^{3}
0.001	4.2×10^{2}	4.5×10^{3}
0.0001	4.2×10^{1}	4.5×10^{3}

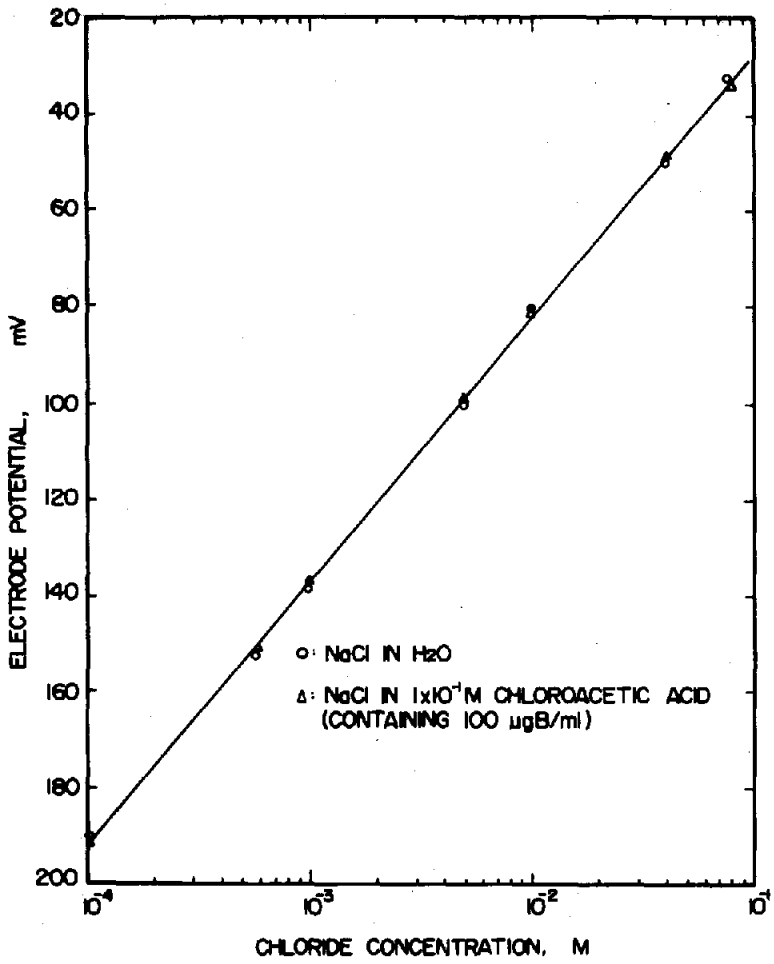

Fig. 1. Calibration curve of chloride concentration *vs.* electrode potential. ○ NaCl in water; △ NaCl in 0.1*M* chloroacetic acid containing 100 μg g boron per ml.

^{4}He)^{7}Li can be obtained by subtracting the chloride concentration in the blank (boron-free chloroacetic acid solution) from that in the sample (chloroacetic acid solution containing boron).

To achieve an accurate determination of chloride by using the chloride-selective electrode, the influence of chloroacetic acid and boron on the measurement must first be assessed. Figure 1 shows the relationship between chloride concentration and electrode potential. Clearly no interference can be observed in the presence of chloroacetic acid (0.1*M*) and sodium borate (B 100 μg/ml).

A plot of boron concentration against the concentration of chloride ions produced by fission radiation was constructed. Figure 2 demonstrates the relationship between the yield of chloride ions by fission radiation and the boron content in irradiated solutions containing various concentrations of chloroacetic acid. The results show that the yield of chloride ions by fission radiation is linearly proportional to the concentration of boron down to 10^{-5} g/ml. The figure also shows that the yield of chloride ions by fission radiation increases with increasing concentration of chloroacetic acid solution. A concentration around 0.1*M* is suitable for practical purposes.

The effect of irradiation time on the response curve was also examined. From Fig. 3 it can be seen that longer irradiation times are more favourable than shorter ones for the production of chloride. They will, however, create more complications in the system owing to the subsequent reactions of the radiolysed products. An irradiation time of around 1 min was considered to be suitable in this study.

The limits of detection and the precision of determination of boron must be considered. Table 2 summarizes the results for both samples (with various boron contents) and blanks (without boron) in 0.3*M* chloroacetic acid, irradiated for 30 sec. It can be seen from Table 2 that the potential reading for the blank is low compared with that for the samples, owing

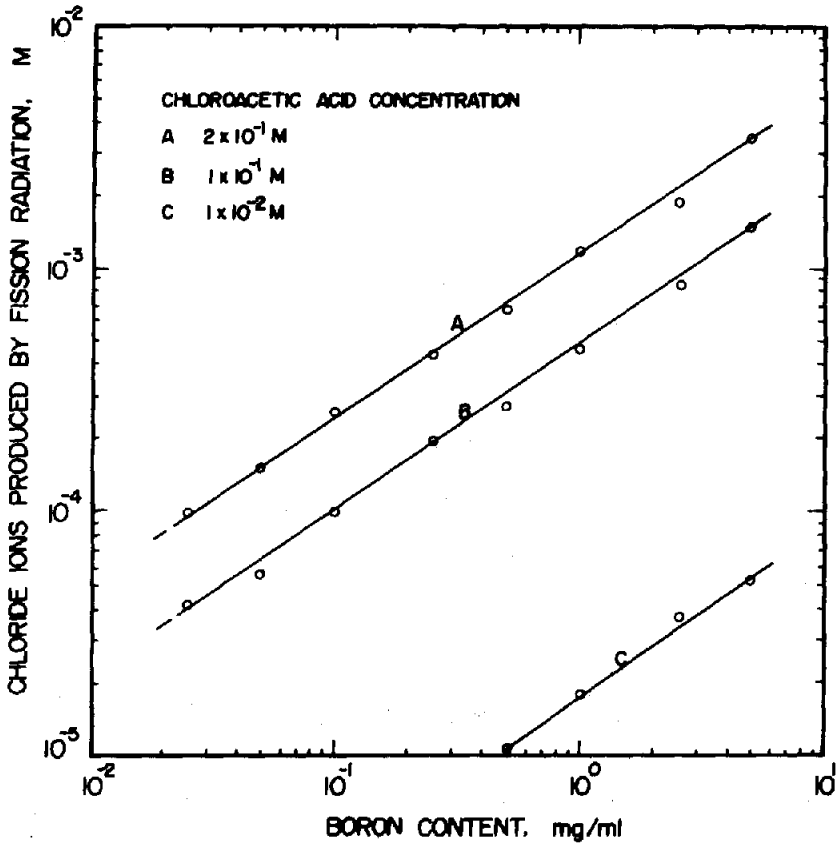

Fig. 2. Relationship between the yield of chloride ions by fission radiation and the boron in the irradiated solutions containing various concentrations of chloroacetic acid: A, 0.2*M*; B, 0.1*M*; C, 0.01*M*. Irradiation time 1 min.

to the strong concomitant radiation field in the reactor. The difference in potential readings between sample and blank is very small when the boron content is low. Since the ion-selective electrode gives a logarithmic relation of response to concentration (as can be seen from Fig. 1), a very small change in chloride ion concentration at a high chloride ion concentration can not be determined with high precision. The standard deviation (Table 2) increases with decreasing concentrations of boron. With the present experimental conditions boron concentrations down to 20 μg/ml can be determined with reasonable precision (relative standard deviation 16%).

The interference of halides and some common ions in the determination of chloride ions is summarized in Table 3. As can be seen, for some common ions such as Na^+, K^+, Mg^{2+}, NO_3^-, Ca^{2+}, PO_4^{3-}, no interference is observed at concentrations up to 0.1*M*. Halide ions, (except F^-), show serious interference even at concentrations as low as $10^{-4}M$. Metal ions, such as Hg^{2+}, Ag^+, Cu^{2+}, which form strong complexes with chloride,[16] interfere to some extent in the precise determination of chloride ions as can be seen from Fig. 4. The interference from Hg^{2+} and Ag^+ begins at the μg/ml concentration level, while that from Cu^{2+} begins at about 10^2 μg/ml. No interference can be observed for Cd^{2+}, Zn^{2+}, Ni^{2+} or other ions with less tendency to complex with chloride.

Several attempts have been made to eliminate the interfering ions mentioned above. Experimental evidence shows that the interference of halide ions can be eliminated either by the addition of a substoichiometric amount of silver nitrate prior to the irradiation, or by evaporating the sample to dryness in the presence of nitric acid. The interference of metal ions can be eliminated by extracting the sample solution with sodium diethyldithiocarbamate in chloroform at pH 2–3. Table 4 shows evidence of the elimination of the interferences of Hg^{2+}, Ag^+, Cl^- and Br^-, each ion being present at a concentration of 50 μg/ml in the solution for pretreatment.

The applicability of the method to the determination of boron has been tested with natural water samples and biological materials. Pretreatment of the water sample was by sodium diethyldithiocarbamate extraction followed by addition of chloroacetic acid,

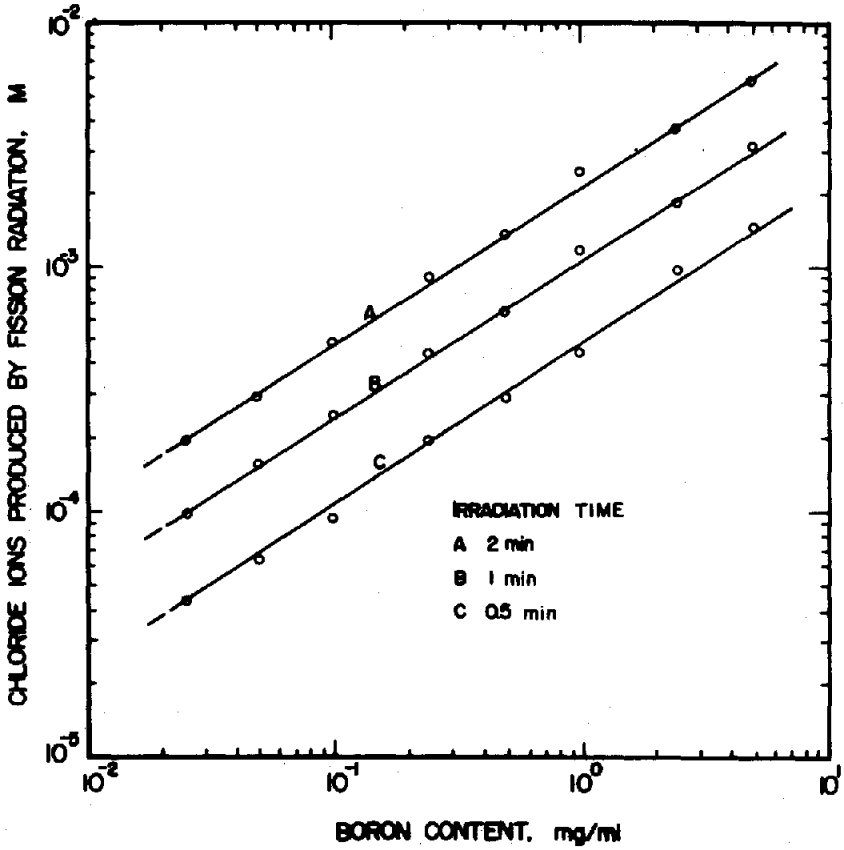

Fig. 3. Relationship between the yield of chloride ions by fission radiation and the boron content in the irradiated solutions for different irradiation times: A, 2 min; B, 1 min, C, 0.5 min. Chloroacetic acid concentration 0.2*M*.

Table 2. Precision of the method

B content, *mg/ml*	Electrode reading, *mV*	Total [Cl^-], $10^{-3}M$	Net [Cl^-] produced by fision radiation, $10^{-4}M$ Individual determination	Average	Standard deviation*
0 (Blank)	139.2	0.963			
	139.5	0.940	—	—	—
	140.2	0.892			0.892flh9
		Av. 0.932			
5.0	99.2	5.26	42.1	—	—
1.0	120.5	2.13	12.3	—	—
0.25	128.5	1.51	5.84	5.42	0.47 (9%)
	128.7	1.41	5.68		
	129.8	1.50	4.82		
	128.8	1.45	5.18		
0.10	132.0	1.28	3.48	3.20	0.39 (12%)
	133.4	1.21	2.82		
	131.8	1.29	3.62		
	133.0	1.23	3.00		
0.02	135.5	1.11	1.78	1.48	0.24 (16%)
	135.8	1.08	1.52		
	136.5	1.05	1.20		
	135.8	1.08	1.52		
0.01	138.0	1.00	0.71	0.81	0.31 (35%)
	136.5	1.05	1.18		
	137.8	0.99	0.60		
	138.0	1.00	0.71		

* Relative standard deviation in brackets.

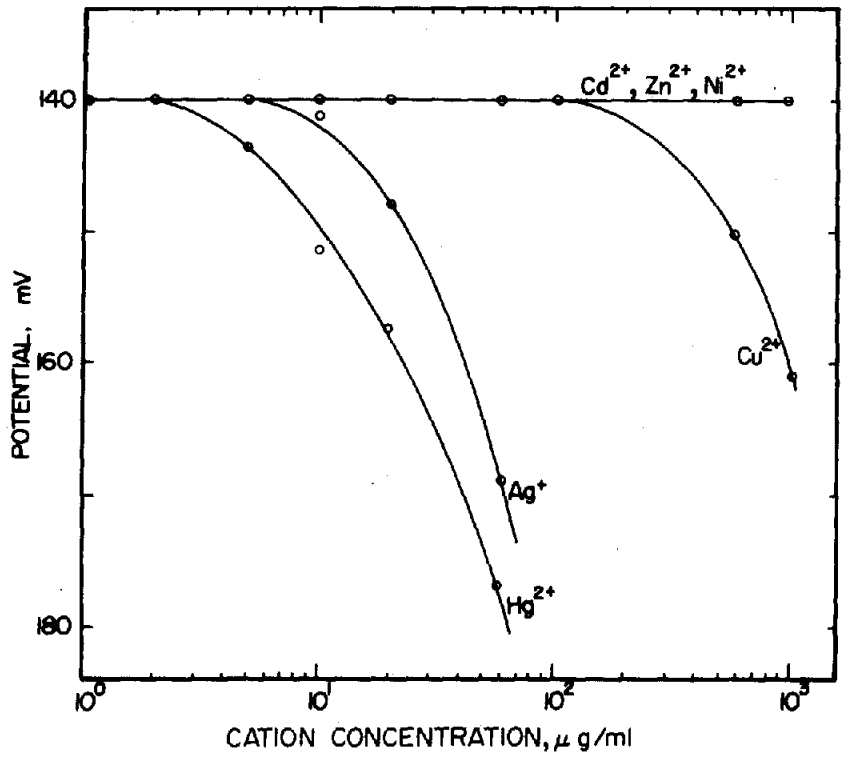

Fig. 4. Effect of concentration of metal ions (forming negatively-charged complex ions with chloride) on the measurement of electrode potential. Concentration of chloride ion $1 \times 10^{-3}M$ in $0.1M$ chloroacetic acid.

while that of the orchard leaves (NBS standard reference material) was by digestion with nitric acid and hydrogen perioxide followed by distillation of boron as methyl borate.

The boron content of the two samples is given in Table 5. The same samples were analysed for boron content by the standard colorimetric method using carmine.[17] The values obtained by the two methods are found to be in good agreement. The accuracy of this method is confirmed by the good agreement between the experimental data and the NBS certified value for orchard leaves.

Two factors dominate the present method for the determination of boron: the amounts of thermal-neutron flux effective for the irradiation of the sample and the ratio of the thermal-neutron flux to the concomitant radiation dose in the reactor.

An increase in thermal-neutron flux of an order of magnitude would, in principle, increase tenfold the concentration of chloride ions produced by the fission radiation and thus decrease the detection limit for

Table 3. Effect of various ions on the determination of halide ion with the chloride-selective electrode (chloroacetic acid $0.2M$, irradiation time 2 min; boron 100 μg/ml)

Ion	Concentration, M	Electrode reading, mV
—	—	95.6
Mg^{2+}	1×10^{-2}	96.1
Na^{+}	2×10^{-1}	95.8
K^{+}	2×10^{-1}	95.7
Ca^{2+}	1×10^{-2}	95.4
NO_3^-	2×10^{-2}	96.1
SO_4^{2-}	1×10^{-2}	95.4
PO_4^{3-}	1×10^{-2}	96.0
F^-	1×10^{-2}	95.6
Cl^-	1×10^{-5}	95.1
	1×10^{-4}	88.4*
Br^-	1×10^{-5}	94.8
	1×10^{-4}	88.8*
I^-	1×10^{-5}	94.2
	1×10^{-4}	89.3*

* Interference is observed

Table 4. Elimination of the interference of Hg^{2+}, Ag^{2+}, Cl^- and Br^- (chloroacetic acid $0.2M$; boron 100 μg/ml, interfering ion 50 μg/ml; irradiation time 2 min)

Analysis No.	Each interfering ion added, μg/ml	Potential reading, mV
1	50	95.5
2	50	96.0
3	50	96.2
Blank	0	95.6

Table 5. Determination of boron in waste-water and NBS orchard leaves

Sample	Analytical method	Boron, *ppM* Individual			Average
Waste-water	Present*	1.19	1.51	1.58	1.42 ± 0.13
		1.68	1.31	1.26	
	Colorimetric	1.46	1.38	1.59	1.48 ± 0.08
Orchard leaves† (NBS SRM 1571)	Present‡	28.1	35.6	29.8	31.2 ± 2.8
	Colorimetric	33.2	31.8	32.5	32.5 ± 0.50

* 100 ml of water taken and concentrated to 5 ml for neutron irradiation.
† NBS certified value is 33 ± 3 ppM (ng/g).
‡ 2 g of orchard leaves taken for each analysis.

boron. Decreasing concomitant radiation, on the other hand, will lower the chloride concentration of the blank and increase the difference in chloride concentration between blank and sample, consequently increasing the precision of the determination. Both thermal-neutron flux and concomitant radiation dose are, however, characteristic of a nuclear reactor. In our present study, under the fixed irradiation condition, (thermal-neutron flux 2×10^{12} $n.cm^{-2}.sec^{-1}$, concomitant radiation dose 4.5×10^3 rad/sec), boron down to about 10^{-5}g/ml can be determined with good reproducibility.

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TRENNUNG UND BESTIMMUNG DER EINZELNEN EISENSPEZIES IN WÄSSRIGER LÖSUNG MIT HILFE DER ELEKTROPHORESE UNTER SCHUTZGASATMOSPHÄRE*

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Zusammenfassung—Die Elektrophorese unter Schutzgasatmosphäre und Verwendung von CDTA als Hilfskomplexbildner im Grundelektrolyten gestattet die Trennung des gelösten Fe(II) und Fe(III) sowie des kolloidalen bzw. ungelösten Fe(III) in Lösungen, die starke Komplexbildner bzw. Mikroorganismen enthalten. Die anschließende Bestimmung der getrennten Eisenspezies kann entweder nach Elution mittels UV-Photometrie bzw. Atomabsorptionsspektroskopie oder direktphotometrisch über Extinktions–Orts-Kurven erfolgen. Das Verfahren ist gut geeignet zur Bestimmung der Eisenspezies in synthetischen bakterienhaltigen Nährlösungen sowie in natürlichen Wässern.

Die Kenntnis des Gehaltes an gelöstem Fe(II) und Fe(III) sowie kolloidalem bzw. ungelöstem Fe(III) ist bei Fragen der Trinkwasseraufbereitung, der Lagerstättenbildung und der Drainierung dauerfeuchter Böden, denen eisenhaltiges Wasser entzogen wird, von erheblicher Bedeutung. Der "Verockerung" der Drainageleitungen versucht man durch deren Einbettung in Reisig, das Komplexbildner abgibt, vorzubeugen. Die betreffenden oft über eine Eigenfärbung verfügenden Grund- und Oberflächenwässer enthalten meist starke, reduzierend wirkende Komplexbildner, daneben manchmal Mikroorganismen, die verallgemeinernd als "Eisenbakterien" bezeichnet werden.[1–3] Aus diesem Grund ist eine Bestimmung der einzelnen Eisenspezies in diesen Wässern mit den in der Literatur beschriebenen Verfahren oft nicht möglich. Es läßt sich nur der Gesamteisengehalt genau ermitteln.

In dieser Arbeit wird ein neues Verfahren zur Trennung der Eisenspezies mit Hilfe der Elektrophorese auf Papier bzw. Celluloseacetatfolie beschrieben.

Um Störungen durch die in den Proben enthaltenen Komplexbildner zu vermeiden, dient Cyclohexylen-1,2-dinitrilotetraessigsäure (CDTA) als Hilfskomplexbildner im Grundelektrolyten. CDTA bildet sowohl mit Fe(II) als auch Fe(III) so starke Komplexe, daß jeweils für eine Oxidationsstufe nur eine Zone auf dem Pherogramm erscheint.

Da der Fe(II)–CDTA-Komplex an der Luft sehr schnell zum entsprechenden Fe(III)-Komplex oxidiert wird, muß die Elektrophorese unter Schutzgasatmosphäre durchgeführt werden. Die Bestimmung der getrennten Eisenspezies erfolgt anschließend entweder nach Elution mittels UV-Photometrie bzw. Atomabsorptionsspektroskopie oder direktphotometrisch über Extinktions–Orts-Kurven.

* Für finanzielle Unterstützung danken wir der Deutschen Forschungsgemeinschaft, Bonn–Bad Godesberg.

EXPERIMENTELLER TEIL

Handelsübliche Chemikalien und Geräte

$^{59}FeSO_4$ *24,6 mCi/g.* Amersham Buchler GmbH (Braunschweig).

Thiobacillus ferrooxidans, *Stamm-Nr. 583.* Deutsche Sammlung für Mikroorganismen (München).

Übrige Substanzen. Präparate (p.a.) von Merck–Schuchardt (Darmstadt).

Stickstoff 4,5 (99,995 % N_2). Messer Griesheim (Frankfurt).

Elektrophorese. Netzgerät Typ NSHK BN 645 Knott (München); Ultrathermostat, Typ K-40 SW, Meßgerätewerk (Lauda); Papier 2043 bMgl Schleicher und Schüll (Dassel); Celluloseacetatfolien SM 11200 Sartorius (Göttingen).

Absorptionsspektren. Doppelstrahlphotometer DK 2A Beckman (München).

Photometrie. Einstrahl-Spektralphotometer PMQ II mit Transmission-Konzentration-Rechner und Digitalanzeige Zeiss (Oberkochen); Quarzküvette 114-QS, 1,00 cm.

Atomabsorptionsspektroskopie. Photometer PMQ II mit Flammenansatz FA 1 Zeiss (Oberkochen).

Aktivitätsverteilungskurven. Strahlenmeßplatz LB 241 Laboratorium Prof. Dr. Berthold (Wildbad); Radiopapierchromatograph FH 452 mit zwei Geiger-Müller-Endfensterzählrohren FHZ 15 a in 4 π-Stellung Frieseke u. Hoepfner (Erlangen).

Trennapparatur

Die neuentwickelte Apparatur besitzt ein geringes Totvolumen. Im Unterschied zu handelsüblichen Geräten können die Proben ohne Öffnen der Kammer mit einer Hamiltonspritze während des Spülens mit Schutzgas direkt auf den Träger aufgegeben werden. Die im Grundelektrolyten gelöste Luft entfernt man vor der Trennung durch Evakuieren im Wasserstrahlvakuum. Abbildung 1 zeigt einen Längsschnitt durch die Apparatur.

Auf eine PVC-Kammer (330 × 315 × 90 mm) wird mit Hilfe von 12 Schnappverschlüssen eine Plexiglasplatte mit 9 Septa gepresst. Ein Dichtungsring verhindert das Eindringen von Luft während des Spülvorgangs und der Trennung.

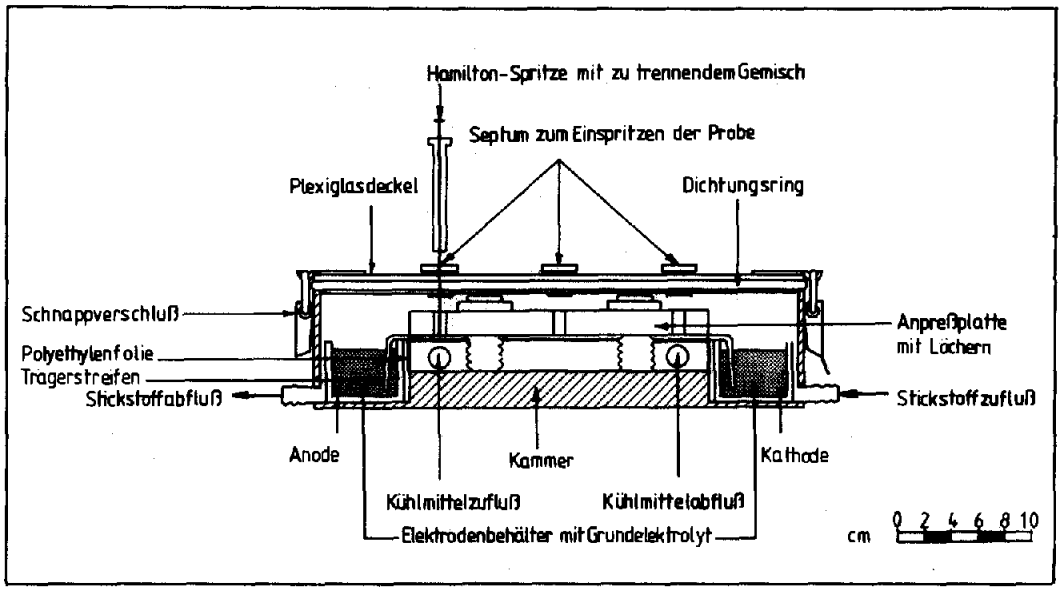

Abb. 1. Schnitt durch die Apparatur.

Die Kühlung erfolgt über einen Metallkühlblock[4] (hier 250 × 200 mm). Den Träger preßt man auf den Kühlblock mit Hilfe einer PVC-Anpressplatte. Diese enthält 9 Bohrungen, die unter den Septa der Plexiglasplatte angeordnet sind.

Durch das Rohr für den Schutzgas-Zufluß spült man vor Probenaufgabe 50 min mit Stickstoff 4,5 (Durchsatz etwa 1 l/min). Er wird vor Eintritt in die Kammer zur Entfernung von noch vorhandenen Sauerstoff-Spuren durch eine alkalische Pyrogallol-Lösung geleitet. Der anodisch gebildete Sauerstoff entweicht auf dem kürzesten Weg aus der Kammer, ohne mit dem zu trennenden Gemisch in Berührung zu kommen.

Vorbereitung des Trägers

Die Papierstreifen werden in den Grundelektrolyten getaucht und mittels einer Walzenpresse von der überschüssigen Lösung befreit.

Die Celluloseacetatfolien dürfen nicht mit den Fingern sondern nur mit einer Pinzette berührt werden. Zur Imprägnierung läßt man die Folie flach auf der Oberfläche der Grundelektrolytlösung schwimmen. Die durch Kapillarwirkung verursachte Benetzung verhindert Lufteinschlüsse in den Poren. Erst nachdem die Folie vollständig von unten benetzt ist, taucht man sie ganz in die Grundelektrolytlösung. Überschüssige Lösung wird mit Filterpapier von der Folie entfernt und diese sofort auf den kalten Kühlblock gelegt, um Verdunstung zu vermeiden. Die Verbindung zu den Elektrodenbehältern wird über Elektrophoresepapierstücke, die mit Grundelektrolyt getränkt sind, hergestellt.

Arbeitsvorschrift—UV Spektrophotometrie

Nach Trennung Papierstreifen der Apparatur entnehmen und 5 min bei 100° im Trockenschrank auf einer Glasplatte trocknen. Berühren der Pherogramme mit metallhaltigen Gegenständen vermeiden. Zur Photometrie beide dunkle $[FeCDTA]^-$-Zonen unter UV-Lampe als Löschflecke lokalisieren. Zonen aus dem Pherogramm ausschneiden (25 mm × 15 mm) und in 25-ml Bechergläser einlegen. Unter gelegentlichem Schütteln mit 1,5 ml dest. Wasser 15 min eluieren. Eluat in 1-cm Quarzküvette füllen und Extinktionen bei 262 nm und Spaltgröße 3,5 mm × 0,01 mm gegen dest. Wasser messen.

Arbeitsvorschrift—AAS

Zur Bestimmung durch Atomabsorptionsspektroskopie die beiden anodischen Zonen mit 1 ml dest. Wasser eluieren. Am Startpunkt zurückgebliebene Zone von ungelöstem Fe(III) mit 1 ml 2*M* Salzsäure 15 min unter gelegentlichem Schütteln lösen. Mit Eisenhohlkathodenlampe bei 248,3 nm und Spaltbreite von 0,03 mm messen. Acetylen–Luft-Gemisch als Brenngas verwenden. Nullpunkt mit Eluat einer Leerzone einstellen.

Tabelle 1. Optimale Trennbedingungen

Trennbedingung	A	B
Träger	Papier	Celluloseacetat
Grundelektrolyt	0,1*M* CDTA in 0,4*M* NaOH pH 11,1	0,1*M* CDTA in 0,25*M* NaOH pH 6,5
Schutzgas	N_2 4,5	N_2 4,5
Vorspülzeit, *min*	50	50
Probenvolumen, *µl*	10	10
Spannung, *V*	2000	2000
Stromstärke, *mA*	25	10
Trenndauer, *min*	30	15
Temperatur, °C	−4	−4

Tabelle 2. Störung durch Komplexbildner bei Trennbedingungen A bzw. B

Komplexbildner	Molverhältnis Fe(III):Komplexbildner	Trennbedingung A	B
Oxalat	1:3	+	−
Tartrat	1:2	+	−
Citrat	1:2	+	−
Gallussäure	1:2	+	+
Tannin	—	+	+
Protocatechusäure: L-Leucin = 1:2	1:3	+	−
Thiocyanat	1:6	+	+
Cyanid	1:6	−	−

+: keine Störung.
−: Störung.

Arbeitsvorschrift—direkt photometrie

Sofort nach Trennung Celluloseacetatfolie der Apparatur entnehmen und durch Abrollen mit Spezialroller bzw. Reagenzglas luftblasenfrei auf Quarzplatte aufziehen. Antrocknen der Folie vermeiden. Quarzplatte mit Celluloseacetatfolie 5 min in Transparenzbad ruhig liegen lassen. Nach Ablaufen der überschüssigen Transparenzlösung Quarzplatte mit Folie im Trockenschrank bei 100° trocknen. Leichte Trübung des transparenten Films, hervorgerufen durch den Grundelektrolyten, stört bei der Auswertung nicht. Extinktions–Orts-Kurven bei 262 nm aufnehmen. Pherogrammtransport-und Schreibergeschwindigkeit 2 cm/min, Meßflächendimension 3,5 mm × 0,02 mm. Transparenten Film von Quarzplatte durch Einlegen in 50° warmes Wasser ablösen. Vor jeder neuen Verwendung Quarzplatte mit Chromschwefelsäure reinigen.

ERGEBNISSE UND DISKUSSION

Trennung und Bestimmung

Als Trägermaterialien werden Papierstreifen bzw. Celluloseacetatfolien verwendet. Da Celluloseacetat durch OH^--Ionen angegriffen wird, sind Trennungen maximal bis pH 6,5 möglich. Papier besitzt neben der einfachen Handhabung den Vorteil, daß auch alkalische Grundelektrolyte verwendet werden können. Dadurch erhöhen sich die effektiven Stabilitätskonstanten von $[FeCDTA]^{2-}$ und $[FeCDTA]^-$ beträchtlich. Die Trenndauer ist gegenüber den Celluloseacetatfolien jedoch doppelt so groß und eine photometrische Direktauswertung der Zonen schwieriger. Die am schnellsten wandernde Zone $[FeCDTA]^{2-}$ enthält das gesamte in der Probelösung befindliche Fe(II). Das gelöste Fe(III) bildet eine $[FeCDTA]^-$-Zone mit geringerer Beweglichkeit, während kolloidales bzw. ungelöstes Fe(III) vollständig als Fe(III)-hydroxid ausgefällt wird und am Startpunkt zurückbleibt. Nach Öffnen der Kammer oxidiert die Luft das Fe(II) im $[FeCDTA]^{2-}$-Komplex innerhalb 1 min

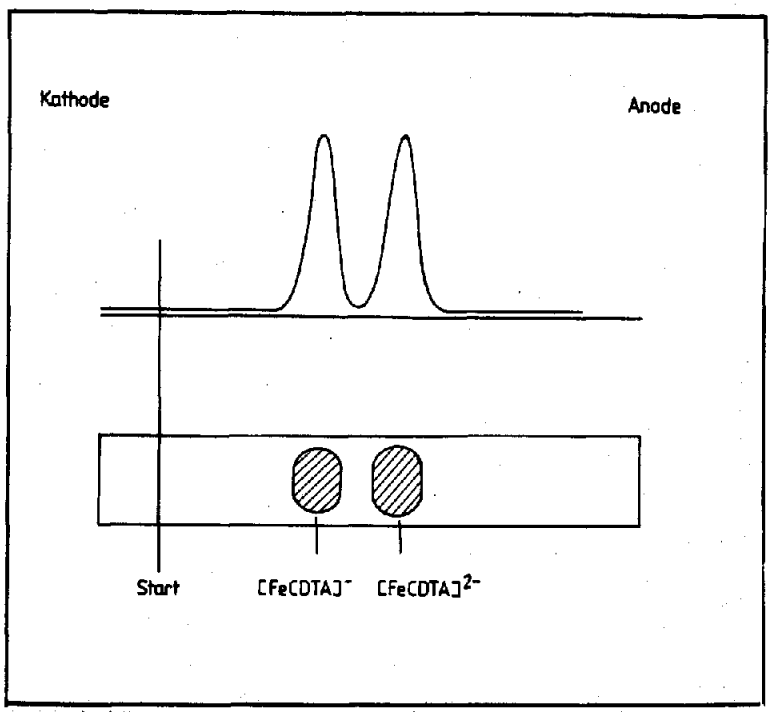

Abb. 2. Fe(II)/Fe(III)-Trennung nach A; oben: Extinktions–Orts-Kurve; unten: Pherogramm unter der UV-Lampe.

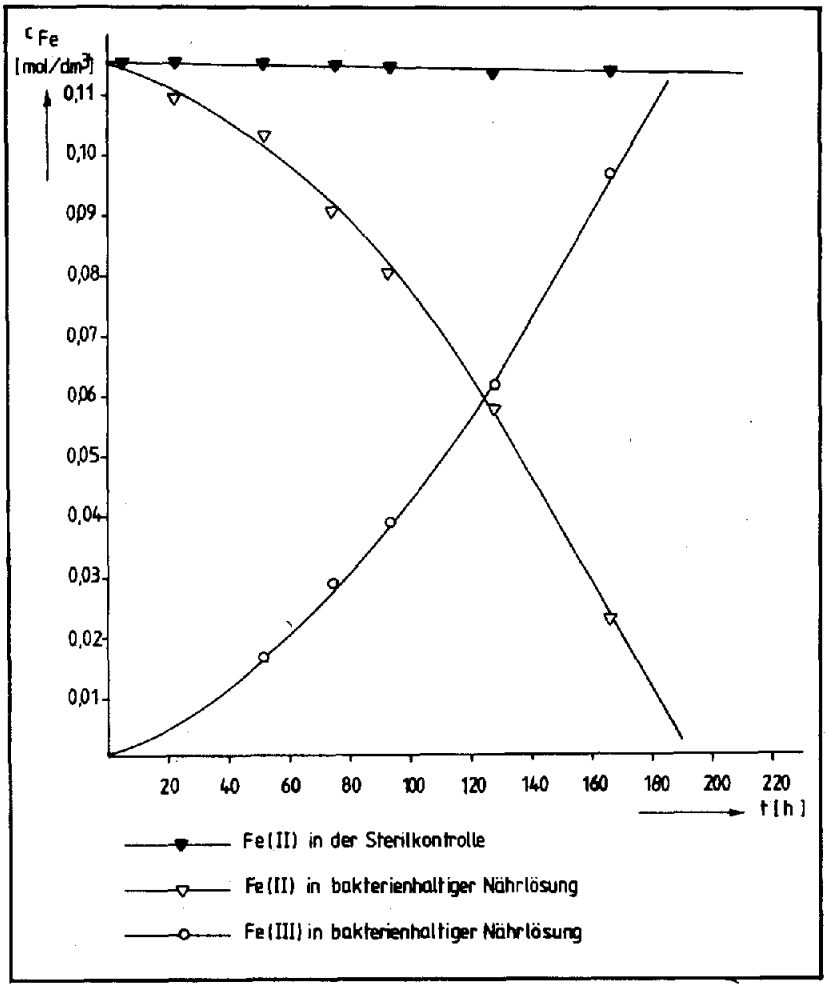

Abb. 3. Fe(II)-Oxidation durch *Thiobacillus ferrooxidans*.

vollständig zu Fe(III). Der Träger enthält somit zwei nebeneinanderliegende gelbe $[FeCDTA]^{2-}$-Zonen, die photometrisch ausgewertet werden.

Die optimalen Trennbedingungen sind in Tab. 1 zusammengestellt. Oberhalb 2000 V reicht die Kühlung zur Abführung der Jouleschen Wärme nicht mehr aus, was zum Durchbrennen der Trägerstreifen führt. Temperaturen $< -4°$ bewirken das Einfrieren des Grundelektrolyten. Nach einer Vorspülzeit von 50 min tritt keine meßbare Fe(II)-Oxidation mehr auf. Bei Trennbedingung B (pH = 6,5) stört eine Anzahl von Komplexbildnern (Tab. 2).

Die Bestimmungen nach Elution setzen Eisenkonzentrationen von mindestens $10^{-4}M$ in der ursprünglichen Probe voraus. Die Genauigkeit bei $10^{-2}M$ Lösung beträgt ±2,5 Rel%. Die Direktphotometrie ist nur bei Eisenkonzentrationen $\geqq 10^{-3}M$ anwendbar. Sie erlaubt lediglich halbquantitative Aussagen.

Zur Bestimmung nach Elution werden die Zonen unter der UV-Lampe durch ihre Löschflecke (Abb. 2 unten) lokalisiert. Die Elution erfolgt anschließend im Falle der $[FeCDTA]^{-}$-Zonen mit Wasser, die Fe(III)-hydroxid-Zone läßt sich nur mit Salzsäure auswaschen. In den Eluaten kann das Eisen entweder durch Atomabsorptionsspektroskopie bei 248,3 nm oder durch UV-Photometrie bei 262 nm, dem Extinktionsmaximum des $[FeCDTA]^{-}$-Komplexes bestimmt werden.

Mit dem direktphotometrischen Verfahren lassen sich nur die gelösten Eisenspezies bestimmen. Hierzu wird die Celluloseacetatfolie durch ein Gemisch von Dioxan:Isobutanol = 7:3 v/v transparent gemacht. Eine Elution durch das Transparenzbad ist nicht festzustellen, wie Versuche mit ^{59}Fe markierten Eisenspezies ergeben. Die Extinktions–Orts-Kurve wird bei 262 nm aufgenommen (Abb. 2 oben).

ANWENDUNGSBEISPIELE

Das neuentwickelte Analysenverfahren erlaubt die Bestimmung der Eisenspezies in Lösungen mit starken Komplexbildnern wie Oxalat, Tartrat, Thiocyanat und Huminsäuren, bakterienhaltigen Nährlösungen, z.B. mit *Thiobacillus ferrooxidans* und natürlichen Wässern.

Tabelle 3. Vergleich der Analysenwerte mit dem Deutschen Einheitsverfahren

	Elektrophorese unter Schutzgasatmosphäre				Deutsches Einheitsverfahren	
	$c_{Fe(II)}$ gelöst mg/l.	$c_{Fe(III)}$ gelöst mg/l.	$c_{Fe(III)}$ ungelöst mg/l.	c_{Fe} gesamt mg/l.	c_{Fe} gesamt mg/l.	$c_{Fe(II,III)}$ gelöst mg/l.
Rohwasser	8,0	5,9	2,0	15,9	15,1	13,5
Sauerbrunnen	19,0	3,0	—	22,0	21,6	21,6

Lösungen mit Oxalat, Tartrat, Thiocyanat bzw. Huminsäuren

Untersucht wird das Redoxverhalten von Fe(II)/Fe(III) in Lösungen mit reduzierenden Komplexbildnern in Gegenwart von Luftsauerstoff. Die Trennung der Eisenspezies wird nach A (Tab. 1) durchgeführt. Die Gesamteisenkonzentration beträgt jeweils $10^{-2}M$, bei Huminsäuren $3.10^{-4}M$.

Beim Schütteln neutraler, oxalathaltiger Lösungen [Molverhältnis Fe(II):$C_2O_4^{2-}$ = 1:3, pH 7,0] ist Fe(II) bereits nach 15 min vollständig oxidiert. Läßt man die Lösung dagegen ruhig stehen, werden nach 40 min nur etwa 40% oxidiert.

Der Anteil an kolloidalem bzw. ungelöstem Fe(III) nimmt in oxalathaltiger Lösung [Molverhältnis Fe(III):$C_2O_4^{2-}$ – 1:3] ab pH 6 sprunghaft zu. Bei pH 8 liegen etwa nur noch 5% gelöstes Fe(III) vor.

Saure oxalathaltige [Molverhältnis Fe(III):$C_2O_4^{2-}$ = 1:3] bzw. tartrathaltige [Molverhältnis Fe(III):Tartrat = 1:2] Fe(III)-Lösungen sind nur in der Dunkelheit stabil. Unter diffusem Tageslicht tritt innerhalb von 20 h vollständige Reduktion zu Fe(II) ein.

Die Fe(III)-Reduktion in Thiocyanathaltigen schwefelsauren Lösungen [Molverhältnis Fe(III):SCN^- = 1:6] läuft dagegen auch in der Dunkelheit, allerdings nur mit etwa halber Geschwindigkeit als bei Lichteinwirkung ab.

Durch Huminsäuren wird Fe(III) nur teilweise reduziert. Als Beispiel dient synthetische Huminsäurelösung (4 mmole Protocatechusäure und 8 mmole L-Leucin in 1 l. Boratpuffer pH 8) mit anfänglich 223,4 mg gelöstem Fe(III) pro liter. Nach 13-tägiger Belüftung und anschließender Abtrennung von ungelöstem Fe(III) enthält das mit 2*M* Salzsäure auf pH 1,5 angesäuerte Filtrat noch 44,8% Fe(II) und 24,6% Fe(III); der Rest ist ausgefallen.

Nährlösungen mit Thiobacillus ferrooxidans

Fe(II) wird unter den gewählten Versuchsbedingungen durch *Thiobacillus ferrooxidans* innerhalb von etwa 200 h vollständig oxidiert, wie aus dem Vergleich mit der Sterilkontrolle hervorgeht (Abb. 3).

Versuchsdurchführung: 33,3 g $FeSO_4.7H_2O$, 0,4 g KH_2PO_4, 0,4 g $MgSO_4.7H_2O$ und 0,4 g $(NH_4)_2SO_4$ in 1 l. 0,1*N* H_2SO_4 lösen. Die Nährlösung im Autoklaven bei 121° und 2.10^5 Pa 20 min sterilisieren. Es stellt sich pH 1,3–1,4 ein. Je 50 ml Nährlösung einerseits mit 1 ml Suspension des *Thiobacillus ferrooxidans*, andererseits mit 1 ml sterilisiertem dest. Wasser versetzen. Beide Lösungen mittels Schüttelmaschine leicht bei 29° bewegen. Zu bestimmten Zeitpunkten je 10 µl Proben entnehmen und nach A (Tab. 1) auftrennen. Pherogrammzonen in diesem Fall mit 10 ml dest. Wasser eluieren und Eisen mittels Atomabsorptionsspektroskopie bestimmen.

Natürliche Wässer

Untersucht werden das Rohwasser eines Wasserwerkes und das Quellwasser eines Sauerbrunnens. Es ergibt sich gute Übereinstimmung zwischen der Summe der ermittelten Einzelwerte der Eisenspezies und dem nach dem Deutschen Einheitsverfahren[5] bestimmten Gesamteisengehalt (Tab. 3).

Versuchsdurchführung: Wegen der geringen Eisenkonzentrationen fünfmal hintereinander 10 µl der jeweiligen Wasserproben auf die gleiche Stelle des Trägers auftragen. Nach A (Tab. 1) auftrennen. Anodische Pherogrammzonen in diesen Fällen mit 0,5 ml Wasser, das am Startpunkt zurückbleibende Fe(III)-hydroxid mit 0,5 ml 2*M* Salzsäure eluieren, Eisen mittels Atomabsorptionsspektroskopie bestimmen.

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Summary—Electrophoresis in an inert atmosphere with CDTA as complexing agent in the electrolyte system permits the separation of dissolved Fe(II) and Fe(III) as well as that of the colloidal and undissolved Fe(III) in solutions containing strong complexing agents or micro-organisms. The separated iron species are subsequently determined by spectrophotometry or by atomic-absorption spectroscopy after elution, or by direct photometry, plotting absorbance as a function of distance along the electrophoretogram. The method is suitable for the determination of the iron in two oxidation states in synthetic nutritive fluids containing bacteria as well as in natural waters.

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A UNIFIED APPROACH TO GLASS ELECTRODE THEORY

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Summary—A unified derivation of ion-exchange theories and "*n*-type" descriptions of glass-membrane potentials is presented. A review and comparison of the existing theories of glass electrodes is given on this basis. Nearly all of the earlier approaches correspond to or follow from special cases of the present theory. For general practical applications the following simple equation is suggested, which incorporates the familiar Eisenman equation and Nikolskii's results for heterogeneous-site glasses:

$$E = \text{const} - RT/F \ln \sum_i \beta_i [(a'_H)^{1/n_i} + (K_i a'_M)^{1/n_i}]^{-n_i}$$

where E is the emf, a'_H and a'_M are the cation activities in the sample solution, and K_i, β_i, and n_i are the selectivity-determining parameters for sites i in the glass membrane. The published response of Na_2O–Al_2O_3–SiO_2 glasses is used to test this equation; the results are compared with different extensions of glass-electrode theory.

Since the nineteen-thirties, many different theories have been devoted to the interpretation of glass-membrane potentials (for reviews, see references 1–3). These approaches may be classified according to their conceptual features, into the following categories.

(*a*) Simple ion-exchange theories, assuming homogeneous properties and idealized behaviour of the glass membrane.[4–6]

(*b*) Modifications correcting for the non-ideality of the glass phase,[7–13] preferably by invoking an *n*-type description of ion activities.[9,14]

(*c*) Solid-state approaches that account for multiple cation-exchange sites of different bonding strengths (heterogeneous-site glasses).[3,15]

(*d*) Theories related to the concepts for liquid membranes, treating anionic sites (vacancies) as discrete ligands for cations.[16–18]

To elucidate the parallels as well as the discrepancies between the models, a unified description of the glass-membrane potential has been attempted. Nearly all of the theories in groups (*a*)–(*c*) follow from this derivation and correspond essentially to special cases. A more universal, but still clear, formula for the emf-response can be obtained by combining Eisenman's so-called *n*-type description of homogeneous glass membranes[9–12] and Nikolskii's first ion-exchange theory for heterogeneous-site glasses.[2,15] This new approach turns out to be equivalent to a more complicated theory offered by Buck.[3]

THEORY

The ion-specific behaviour of glass electrodes is largely determined by the cation-exchange equilibria established between the R_i^- sites of the glass phase [e.g., $(SiO_{3/2})O^-$ or $(AlO_{4/2})^-$] and the external solution. Here we focus on the selectivity between hydrogen ions H^+ and metal ions M^+, which is governed by equilibria of the type*:

$$HR_i(\text{membrane}) + M^+(\text{solution}) \overset{K_i}{\rightleftharpoons} MR_i(\text{membrane}) + H^+(\text{solution}) \quad (1)$$

By following the suggestion of Rothmund and Kornfeld,[14] which was referred to as *n*-type behaviour of solid ion-exchangers[1,9–12] and corroborated by empirical[1,8,9] and theoretical studies on glass membranes,[7] we obtain the following expression for the law of mass action:

$$K_i = \frac{a'_H (N_{iM})^{n_{iM}}}{a'_M (N_{iH})^{n_{iH}}} \quad (2)$$

where a'_H and a'_M are the activities of H^+ and M^+ in the external solution (sample), and N_{iH} and N_{iM} the mole fractions of sites R_i^- in the glass surface occupied by ions H^+ and M^+, respectively. The coefficients n_{iH} and n_{iM} are associated with the interchange energy and the co-ordination numbers of the cations;[7] in the original work by Rothmund and Kornfeld[14] they were assumed to be identical, which corresponds to a regular-solution approach to the glass phase[19] (see also reference 20). Equation (2) implies that the activities of exchangeable ions from sites R_i^- can be generally formulated as

$$a_{iH} = \alpha_{iH}(N_{iH})^{n_{iH}}; \; a_{iM} = \alpha_{iM}(N_{iM})^{n_{iM}} \quad (3)$$

* The theory evolved in this work can be applied to any pair of univalent cations by simply inserting the corresponding symbols instead of H^+ and M^+. For simplicity, the subscript HM to the ion-exchange constant K_i^- has been omitted.

whereas the concentrations of the same species are obviously given by

$$c_{iH} = N_{iH}C; \quad c_{iM} = N_{iM}C \tag{4}$$

$$N_{iH} + N_{iM} = N_i^{tot} \tag{5}$$

where the activity coefficients α_{iH} and α_{iM} characterize the bonding strength for the given cations in the ionogenic groups, and C is the total concentration of all ion-exchange sites in the glass. Assuming equilibrium distribution of free cations across the membrane/solution interface, the activities a_{iH} and a_{iM} are related to the external activities a'_H and a'_M as follows:

$$\frac{a_{iM}}{a_{iH}} = \frac{k_M a'_M}{k_H a'_H} \tag{6}$$

where k_H and k_M are the ionic distribution coefficients characteristic of the "solvated" rather than the bound cations within the glass. In contrast to the ratio k_M/k_H, the ion-exchange constant K_i evidently includes terms for both ionic distribution and ion binding since we find from equations (2), (3) and (6) that

$$K_i = \frac{k_M \alpha_{iH}}{k_H \alpha_{iM}}. \tag{7}$$

Combination of equations (3) and (5)–(7) leads to the following relationship which, in principle, allows determination of all the individual ion activities established in the surface layer of the glass membrane:

$$\left(\frac{a_{iH}}{\alpha_{iH}}\right)^{1/n_{iH}} + \left(\frac{a_{iH}}{\alpha_{iH}} \cdot K_i \frac{a'_M}{a'_H}\right)^{1/n_{iM}} = N_i^{tot}. \tag{8}$$

In general, glass mixtures may contain N different sorts of ionogenic groups R_i^-, each of which exhibits a different bonding strength for H^+ ions and other cations, M^+. This inhomogeneity of ion binding in the glass was first treated quantitatively in one version of Nikolskii's theories, published in 1953.[15] It was assumed that the total activities a_H and a_M of ions H^+ and M^+ in the glass boundary are the sum of the partial activities a_{iH} and a_{iM}, respectively, contributed by each ionogenic group:

$$a_H = \sum_{i=1}^{N} a_{iH}; \quad a_M = \sum_{i=1}^{N} a_{iM}. \tag{9}$$

These total ion activities are related to the interfacial electrical potential difference $\phi - \phi'$ as follows:

$$\phi - \phi' = \frac{RT}{F} \ln \frac{k_H a'_H}{a_H} = \frac{RT}{F} \ln \frac{k_M a'_M}{a_M} \tag{10}$$

where ϕ' and a' refer to the external solution (sample), and ϕ and a refer to the membrane boundary (at $x = 0$). The system of equations (8) and (10) offers a general theoretical solution for the phase-boundary potential which is presumed to be the dominant contribution to the glass electrode potential. This description encompasses a series of apparently different approaches developed by several pioneers of glass-electrode theory. Some of the corresponding special cases are briefly discussed below.

First, we consider a glass phase that contains only one type of ionogenic site and which approximates ideal behaviour, *i.e.*, $n_H = n_M = 1$. In this case, equation (8) reduces to

$$\frac{a_H}{\alpha_H}\left[1 + K \frac{a'_M}{a'_H}\right] = N^{tot} = 1. \tag{11}$$

Insertion into equation (10) yields:

$$\phi - \phi' = \frac{RT}{F} \ln \frac{k_H}{\alpha_H} + \frac{RT}{F} \ln[a'_H + K a'_M]. \tag{12}$$

If the phase-boundary potential difference between the glass electrode and the sample solution is the only variable contribution to the cell potential E:

$$E = \phi - \phi' + \text{const} \tag{13}$$

we immediately obtain

$$E = \left(\frac{RT}{F} \ln \frac{k_H}{\alpha_H} + \text{const}\right) + \frac{RT}{F} \ln[a'_H + K a'_M]$$

or

$$E = E_H^0 + \frac{RT}{F} \ln[a'_H + K_{HM}^{Pot} a'_M]. \tag{14}$$

Equation (14) offers a rough description, for example, of the "alkali error" (interference by alkali ions) observed for pH-sensitive glass electrodes. Expressions of this type were introduced in 1931–37 by Lark-Horovitz,[4] Dole,[5] and Nikolskii[6] in their pioneering thermodynamic or statistical treatments of the glass-electrode potential, and later found general acceptance in electrode applications.[21] However, the so-called Nikolskii equation, when applied to glass electrodes, often does not agree quantitatively with experimental results. The major discrepancy between this simple theory and experiment is observed in the region of the emf-response function intermediate between the pure H^+ function (for $a'_H \gg K_{HM}^{Pot} a'_M$) and the M^+ function (for $a'_H \ll K_{HM}^{Pot} a'_M$). One possibility for overcoming the problem is to impose an *n*-type description of the membrane activities (see below). A different correction for activity coefficients was proposed by Lengyel *et al.*[13]

In the work by Landqvist[7] and by Schwabe and Dahms,[8] considerations were still restricted to glasses with one ionogenic group. However, the non-ideality of these phases was taken into account, either theoretically[7] or empirically,[8] by introducing individual coefficients n_H and n_M. Equation (8) then retains its general form (for $i = 1$):

$$\left(\frac{a_H}{\alpha_H}\right)^{1/n_H} + \left(\frac{a_H}{\alpha_H}\right)^{1/n_M} \left(K \frac{a'_M}{a'_H}\right)^{1/n_M} = 1. \tag{15}$$

A relationship between the term a_H/α_H and the

electrical potential is obtained from equations (10) and (13):

$$\frac{a_H}{x_H} = \frac{k_H a'_H}{x_H} \exp\left[-\frac{F}{RT}(\phi - \phi')\right] = a'_H \exp\left[-\frac{F}{RT}(E - E^0_H)\right]. \quad (16)$$

This leads to an implicit solution for the observable emf E:

$$(a'_H)^{1/n_H} \exp\left[-\frac{F}{n_H RT}(E - E^0_H)\right] + (K a'_M)^{1/n_M} \exp\left[-\frac{F}{n_M RT}(E - E^0_H)\right] = 1. \quad (17)$$

Landqvist[7] gave his basic result for the deviation of the glass-electrode potential from that expected ideally for the hydrogen half-cell:

$$\Delta E = E - \left(E^0_H + \frac{RT}{F} \ln a'_H\right).$$

Hence:

$$\exp\left(-\frac{F\Delta E}{n_H RT}\right) = 1 - \left[K \frac{a'_M}{a'_H} \exp\left(-\frac{F\Delta E}{RT}\right)\right]^{1/n_M} \quad (18a)$$

An equivalent expression appears in an article by Schwabe and Dahms.[8] Accordingly, equation (17) may be rewritten as

$$\Delta pH + n_M \log(1 - 10^{-\Delta pH/n_H}) = \log\left(K \frac{a'_M}{a'_H}\right) \quad (18b)$$

where

$$\Delta pH = F\Delta E/2.3\,RT.$$

It was shown that equations (18a) and (18b) permit a very close fit to the experimental data obtained for different glass compositions.[7,8] On the other hand, such equations are difficult to handle. A more convenient—and nevertheless successful—description of the emf-response of glass electrodes is based on the assumption that

$$n_H = n_M = n \quad (19)$$

In this case, equation (17) reduces simply to

$$E = E^0_H + \frac{nRT}{F} \ln[(a'_H)^{1/n} + (K a'_M)^{1/n}]. \quad (20)$$

An analogous result was obtained recently for solid-state membrane electrodes where K is identical to the ratio of solubility products for the given species.[22] If formation of a mixed solid phase is hindered, it holds that $n \to 0$, whereas an ideal mixed phase or adsorption isotherm corresponds to $n = 1$.[22] For glass membranes it is very often found that $n > 1$. Equation (20) then predicts a smoother transition from the H^+ function to the M^+ function of the electrode than the unmodified Nikolskii equation (14) does (see Fig. 1).

Equation (20) was extended by Eisenman *et al.*[1,9–12] who also took into account the internal-diffusion potential of the membrane. The theory is based on the Nernst–Planck equation (21a,b) describing the ion fluxes J_H and J_M in the membrane phase:

$$J_H = -u_H c_H \frac{d}{dx}[RT \ln a_H + F\phi] \quad (21a)$$

$$J_M = -u_M c_M \frac{d}{dx}[RT \ln a_M + F\phi]. \quad (21b)$$

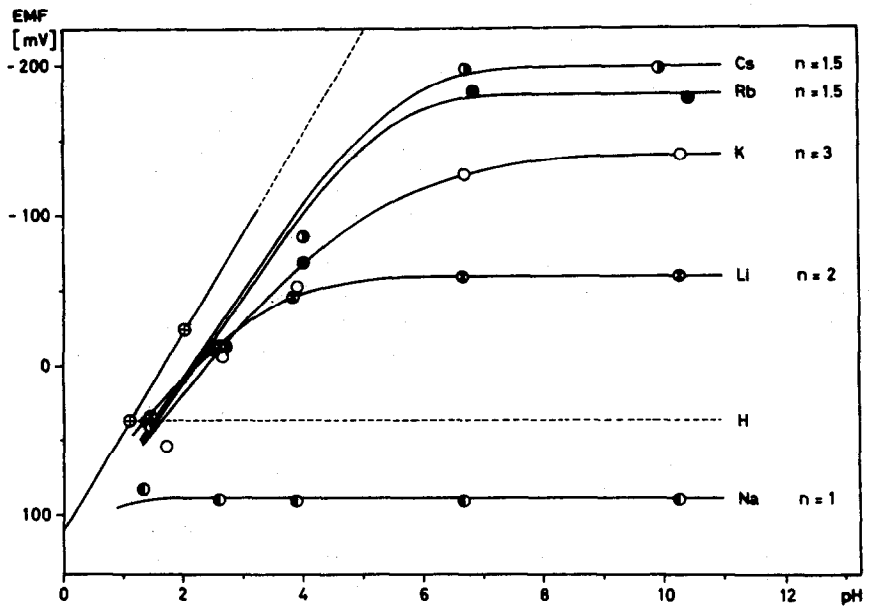

Fig. 1. The pH-response of a sodium-selective glass electrode in the presence of different alkali metal ions (0.1 *M* solutions).[23] The solid lines are drawn according to equations (20) and (26).[23] The experimental points for the larger alkali metal ions indicate some tendency towards a stepwise response function.

Assuming a constant ratio of cation mobilities, u_M/u_H, and recalling equations (3), (4) and (19), we can write:

$$J_H = -u_H CnRT\left[\frac{d}{dx}(N_H) + N_H\frac{F}{nRT}\frac{d\phi}{dx}\right] \quad (22a)$$

$$J_M = -u_H CnRT\left[\frac{d}{dx}\left(\frac{u_M}{u_H}N_M\right) + \frac{u_M}{u_H}N_M\frac{F}{nRT}\frac{d\phi}{dx}\right]. \quad (22b)$$

For zero-current conditions, $J_H + J_M = 0$. Hence

$$\frac{d\phi}{dx} = -\frac{nRT}{F}\frac{d}{dx}\ln\left(N_H + \frac{u_M}{u_H}N_M\right)$$

which upon integration over the membrane interior from $x = 0$ to $x = d$ yields the diffusion potential:

$$E_D = \phi(d) - \phi(0) = \frac{nRT}{F}\ln\frac{N_H(0) + (u_M/u_H)N_M(0)}{N_H(d) + (u_M/u_H)N_M(d)}. \quad (23)$$

The two phase-boundary potentials are given by expressions of the type (10):

$$\phi(0) - \phi' = \frac{RT}{F}\ln\frac{k_H a'_H}{a_H(0)}; \qquad \phi(d) - \phi'' = \frac{RT}{F}\ln\frac{k_H a''_H}{a_H(d)}. \quad (10a, b)$$

Correspondingly, the boundary-potential difference assumes the form [see also equation (3)]:

$$E_B = \phi'' - \phi(d) + \phi(0) - \phi' = \frac{nRT}{F}\ln\frac{(a'_H)^{1/n}/N_H(0)}{(a''_H)^{1/n}/N_H(d)}. \quad (24)$$

The total membrane potential E_M is finally obtained by simply adding equations (23) and (24), making use of (2):

$$E_M = \frac{nRT}{F}\ln\frac{(a'_H)^{1/n} + (u_M/u_H)(Ka'_M)^{1/n}}{(a''_H)^{1/n} + (u_M/u_H)(Ka''_M)^{1/n}}. \quad (25)$$

For membrane electrodes having a constant internal solution, the emf function reduces to:

$$E = E^0_H + \frac{nRT}{F}\ln[(a'_H)^{1/n} + (K^{Pot}_{HM}a'_M)^{1/n}] \quad (26)$$

where $K^{Pot}_{HM} = (u_M/u_H)^n K$. As Eisenman's equation (26) turns out to be formally identical to equation (20), addition of the diffusion potential according to equation (23) has no obvious effect on the shape of the emf response curve*, except for a more general definition of the potentiometric selectivity factor. These findings are in favour of the aforementioned pure ion-exchange concepts of glass-membrane electrodes, an approach which indeed shows good agreement with experiment.[2,7–9,15,16] Nevertheless, Eisenman's equation has probably become the most widely used formula in the field of glass electrodes. It is worthy of note that the ideal form of equation (26) (for $n = 1$, but including the mobility ratio) was published as early as 1931![4]

All the theories discussed so far account for situations where the selectivity behaviour of the glass electrode is dictated by the properties of one ionogenic group. In typical pH-glasses, it is the strongly basic group $(SiO_{3/2})O^-$ that is selectivity-determining, whereas glasses selective for sodium or other cations contain a relatively high concentration of weakly basic groups such as $(AlO_{4/2})^-$. The glass compositions of commercially available electrodes have been optimized and their response can be approximately described on the basis of equations (20) and (26) (see also Fig. 1). For more general cases, however, glasses must be considered to contain a variety of anionic sites ($i = 1, 2, \ldots N$) of different bonding strengths. All these groupings contribute to the ion-exchange properties of the membranes. The potentiometric behaviour of typical heterogeneous-site glasses is characterized by a stepwise response in mixed electrolytes (varying pH at constant pM). A formal description of such behaviour was initiated by Nikolskii.[15] His solution corresponds to equations (8)–(10) of the present generalized ion-exchange theory when the ideality assumption $n_{iH} = n_{iM} = 1$ is used. Thus, in analogy to equation (11):

$$\frac{a_{iH}}{\alpha_{iH}}\left[1 + K_i\frac{a'_M}{a'_H}\right] = N_i^{tot} \quad (27)$$

and hence:

$$a_H = \sum_i a_{iH} = \sum_i \frac{\beta_i a'_H}{a'_H + K_i a'_M}. \quad (28)$$

where

$$\beta_i = \alpha_{iH}N_i^{tot}.$$

Nikolskii's result for the emf function is then readily obtained from equations (10), (13) and (28):

$$E = E^0_H + \frac{RT}{F}\ln\sum_i \beta_i - \frac{RT}{F}\ln\sum_i \frac{\beta_i}{a'_H + K_i a'_M}. \quad (29)$$

This theory has been shown to give a nearly perfect fit for several "normal" potential *vs.* pH curves.[15] The most important consequence, however, is its capability to predict a stepwise response to a'_H at constant a'_M, consisting of regions with Nernstian or near-Nernstian slopes separated by shoulders.[2,15] Formation of such curves requires the presence of at least two sorts of competing ion-exchange sites, having significantly different binding properties [e.g., β_1 and $\beta_2 > 0$ and $K_1 \ll K_2$ in equation (29)]. Since the theoretical curves according to equation (29) did not compare well with all the experimental data, Nikolskii and Shults[16] later developed a second version of the "generalized" theory, which led to somewhat different results (see Appendix).

The aim of the treatment above was to give a unified derivation of earlier approaches to the theory of glass electrodes. In view of general practical applications, it would be of prime interest to arrive at a

* This is no longer true if a more sophisticated model is used to describe the diffusion potential (see Appendix).

formula incorporating Eisenman's familiar n-type description, equations (20) and (26), and Nikolskii's heterogeneous-site theory, equation (29). Such an all-encompassing formula could be found more intuitively, but here it is derived strictly from equations (8)–(10). For simplicity, we make use of (13) and (19):

$$n_{iH} = n_{iM} = n_i \tag{19}$$

The following relations can then be written, in analogy to (8) and (28):

$$\left(\frac{a_{iH}}{\alpha_{iH}}\right)^{1/n_i}\left[1 + \left(K_i \frac{a'_M}{a'_H}\right)^{1/n_i}\right] = N_i^{tot} \tag{30}$$

and

$$a_H = \sum_i a_{iH} = \sum_i \frac{\beta_i a'_H}{[(a'_H)^{1/n_i} + (K_i a'_M)^{1/n_i}]^{n_i}} \tag{31}$$

where

$$\beta_i = \alpha_{iH}(N_i^{tot})^{n_i}.$$

This leads to the final result:

$$E = E_H^0 + \frac{RT}{F}\ln\sum_i \beta_i - \frac{RT}{F}\ln\sum_i \frac{\beta_i}{[(a'_H)^{1/n_i} + (K_i a'_M)^{1/n_i}]^{n_i}}. \tag{32}$$

This generalized formula combines the advantages of Eisenman's equation (variable coefficients n) with those of Nikolskii's result (various sites i). For evident reasons, equation (32) is successful in reconstructing all the response functions that could be obtained from either of these theories. Beyond that, it affords a quantitative description of experimental data in cases where the theories mentioned fail and where other, basically different, models have had to be constructed (see below).

DISCUSSION

Figure 2 illustrates the pH response for a series of sodium aluminosilicate glasses, Na_2O–Al_2O_3–SiO_2 of varying alumina content.[2,16] The potentiometric behaviour of these glasses can be interpreted on the basis of equation (32) if two terms are taken with $K_1 \ll K_2$. The term with $i = 1$ corresponds to the silica sites and gives rise to the sodium error at high pH values, whereas the intermediate step in response arises from the term with $i = 2$, corresponding to the alumina sites. For simplicity, the same values, $n_1 = 5$ and $n_2 = 1$ were used throughout. Hence, the following simplified form of equation (32) was used for all calculations, involving only three adjustable selectivity-parameters:

$$E = E_H^0 + \frac{RT}{F}\ln(\beta + 1) - \frac{RT}{F}\ln\left[\frac{\beta}{[(a'_H)^{0.2} + (K_1 a'_M)^{0.2}]^5} + \frac{1}{a'_H + K_2 a'_M}\right] \tag{32a}$$

with

$$\beta = \beta_1/\beta_2.$$

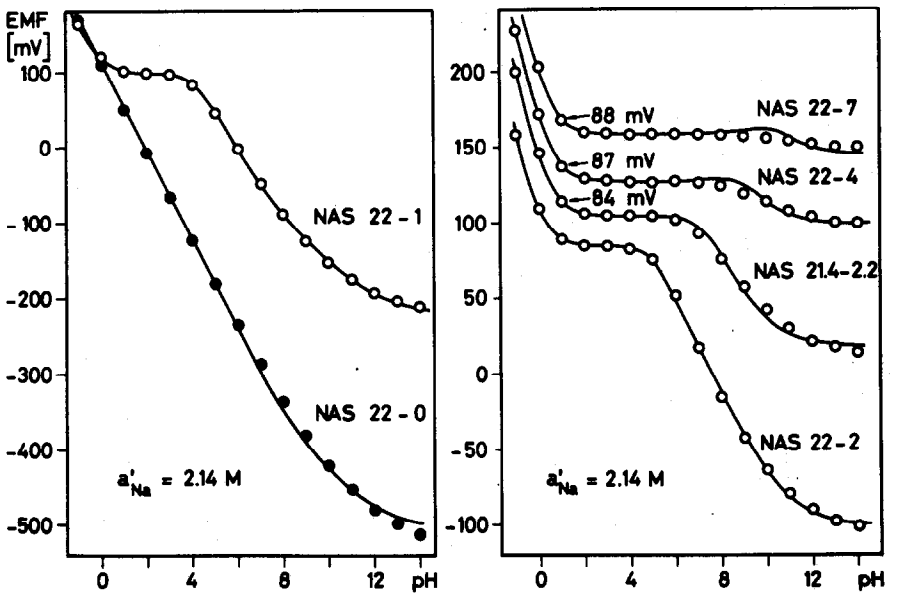

Fig. 2. Computed pH-response of different sodium aluminosilicate glasses at constant sodium background ($c'_{Na} = 3M$, $a'_{Na} = 2.14M$). Circles: values obtained from equation (32a) of this work, using the parameters given in Table 1. Solid lines: values expected from Buck's theory (Appendix and Table 1). Both sets of curves are in agreement with experimental data.[2,3,16] For convenience, some of the curves are shifted vertically, as indicated by the values obtained for pH = 1. The glass numbers denote mole % of Na and Al: NAS 22-0 is a 22% Na_2O–78% SiO_2 glass, NAS 22-1 corresponds to 22% Na_2O–1% Al_2O_3–77% SiO_2, *etc.*

In Fig. 2 emf-values computed according to equation (32a) are compared with curves given by Buck[3] on the basis of a more involved theory (see Table 1 and Appendix). Buck's curves were shown to nearly coincide with the experimental data,[2,3,16] except for the glasses with 4 and 7 mole % Al_2O_3, for which the present theory seems preferable. For glasses with high alumina content, Buck's theory predicts spurious local maxima of the potential *vs.* pH curves[3] (see also Fig. 2) which do not appear in the experimental results.[2,16] Nevertheless, the agreement between the new equations (32) and (32a) and Buck's equation [(A-1)] (see Appendix) is excellent, in spite of the formal differences. For the five Na_2O–Al_2O_3–SiO_2 glasses in Fig. 2, the mean deviation between the two approaches is less than 2 mV. An even better agreement between single curves, especially for the system 22% Na_2O–78% SiO_2, could be achieved by optimizing the parameter n_1 for each glass composition, instead of inserting an average value of $n_1 = 5$.

These results clearly demonstrate the equivalence of equation (32a) and Buck's theory. The advantages of the present treatment are as follows,

(*a*) The compactness and clarity of the basic formula, equation (32), which is a logical extension of more familiar expressions.

(*b*) The comparatively small number of parameters involved (see Table 1).

(*c*) The systematic variation of these parameters with varying glass composition.

Table 1 shows that the selectivity coefficient K_2, characteristic of the alumina sites, remains roughly independent of the membrane composition. In contrast, β is, by definition, a direct measure of the heterogeneity, and the selectivity coefficient K_1 for silica sites also shows a pronounced variation. The last effect is probably caused by the formation of some mixed-type sites, the population of which should increase with decreasing β. In fact, the following relationship was established empirically:

$$K_1 = 4.7 \times 10^{-12} + 3.0 \times 10^{-14}/\beta$$

Estimated and observed values of K_1 agree within a factor of ≤ 2.5 for glasses with 0–4% Al_2O_3, although K_1 varies over a range of 10^4. No such correlation is found for the parameter K_1 used by Buck (see Table 1).

Before the present or Buck's approach, only the "second variant ion-exchange theory" of Nikolskii and Shults[2,16] was capable of fitting part of the curves in Fig. 2. Calculations by Nikolskii and Shults gave a surprisingly good fit of data from 2 to 7% Al_2O_3 by variation of only one parameter (see Appendix), but they failed in the crucial case with 1% Al_2O_3, where the maximal deviations from experiment exceeded 50 mV. Therefore, the use of the present extension of Nikolskii's theory for ternary glasses is to be encouraged.

APPENDIX

Summary of Different Glass Electrode Theories, in Terms of the Present Formulation

The alternative approach by Buck,[3] based on the solid state, does not use *n*-type non-ideality corrections, but in-

Table 1. Fundamental parameters obtained from data fit (Na_2O–Al_2O_3–SiO_2 glasses; varying pH at 3*M* sodium levels)

Al_2O_3, mole %	K_1 (ion-exchange on silica sites)	K_2 (ion-exchange on alumina sites)	k_M/k_H (ion-exchange for solvated ions)	$K_{H/M}$ (mobility and defect generation ratio)	β	E°_H, *mV*
Values from equation (32a) of this work						
0	4.7×10^{-12}	—			$\sim \infty$	110
1	2.0×10^{-10}	0.40			1.45×10^{-4}	103
2	2.8×10^{-9}	0.29			1.9×10^{-5}	97
2.2	1.1×10^{-8}	0.12			4×10^{-6}	110
4	2.2×10^{-8}	0.10			5.5×10^{-7}	117
7	(2.2×10^{-8})*	0.10			(10^{-7})*	118
Values from equation (A-1), according to Buck[3]						
0	2.5×10^{-9}	—		7.8×10^{-3}	$\sim \infty$	~115
1	6.7×10^{-8}	0.40		1.9×10^{-3}	6.7×10^{-5}	103
2	9.7×10^{-7}	0.29		2.4×10^{-3}	6.7×10^{-6}	97
2.2	3.9×10^{-8}	0.12		3.5×10^{-2}	~0	110
4	5.5×10^{-10}	0.10		3.3×10^{-1}	~0	117
7	2.2×10^{-11}	0.12		5.7×10^{-1}	~0	114
Values from equation (A-2), according to Nikolskii and Shults[2,16]						
0	4.1×10^{-13}	—	4.6×10^{-10}		$\sim \infty$	110
1	4.7×10^{-13}	0.47	0.47		10^{-1}	104
2	10^{-11}	0.1	0.1		10^{-4}	124
2.2	10^{-11}	0.1	0.1		10^{-7}	118
4	10^{-11}	0.1	0.1		10^{-9}	118
7	10^{-11}	0.1	0.1		10^{-10}	118

* Different combinations of K_1 and β values led to nearly the same results. For simplicity, the same values K_1 and K_2 were used as for 4% Al_2O_3.

cludes a diffusion potential term. The assumption was made that only a fraction of the interstitial cations (defects) in the glass are mobile and contribute to the diffusion potential. Unfortunately, Buck's derivation is cast in terms of lumped parameters, which makes comparison with other theories difficult. A detailed examination reveals, however, that his basic equation (29)[3] can be transformed into:

$$E = E_H^0 + \frac{RT}{F}\ln(\beta + 1) - \frac{RT}{F}\ln\left[\frac{\beta}{a'_H + K_1 a'_M} + \frac{1}{a'_H + K_2 a'_M}\right] + \frac{RT}{F}\ln\frac{(a'_H)^{1/2} + K_{H/M}(K_1 a'_M)^{1/2}}{(a'_H + K_1 a'_M)^{1/2}}. \quad \text{(A-1)}$$

Evidently, this result corresponds to Nikolskii's interfacial potential, equation (29) for $N = 2$, plus an additional term describing the diffusion potential. The parameter β in equation (A-1) stands for Buck's quantity T_4/α, and $K_{H/M} = T_3\alpha^{1/2}$ represents a new selectivity term, characterizing the ratio of defect generation and mobility of interstitial cations. The parameters are summarized in Table 1. For pure silicate glasses containing only type 1 sites ($\beta \sim \infty$), equation (A-1) reduces to an expression different from Eisenman's equation (20) or (26), and hence gives another meaning to *n*-type behaviour.[3,24] However, *n*-type non-ideality was first observed for purely interfacial phenomena on solid ion-exchangers[14] where diffusion potentials do not come into play.

An approach to heterogeneous-site glasses, based on the liquid state, was initiated by Nikolskii and Shults[2,16] who used a formalism analogous to ordinary solution theory to describe complexation between anionic sites or vacancies and solvated cations in the glass phase. Accordingly, the ion-exchange constant K_i for sites i includes the ratio of complex-formation constants (term α_i in Nikolskii's work) and the ratio of free-cation distribution coefficients, k_M/k_H in our terminology (K_{HM} in Nikolskii's). The following result is obtained when using the assumptions of nearly complete association, zero diffusion potential, and ideal behaviour [for consistency with equations (32a) and (A-1), the subscript 1 is used for silica sites and 2 for alumina sites]:

$$E = E_H^0 + \frac{RT}{2F}\ln(\beta + 1) + \frac{RT}{2F}\ln[a'_H + (k_M/k_H)a'_M] - \frac{RT}{2F}\ln\left[\frac{\beta}{a'_H + K_1 a'_M} + \frac{1}{a'_H + K_2 a'_M}\right]. \quad \text{(A-2)}$$

The numerical parameters of equation (A-1) for the system Na_2O–Al_2O_3–SiO_2 are also included in Table 1. Constancy of selectivity coefficients for glasses with 2–7% Al_2O_3 is most remarkable, but values for 1% Al_2O_3 are based on a very poor fit of experimental data, and an enormous decrease in k_M/k_H (by a factor of 10^9) is required for rationalizing the pH-response of pure silicate glasses. More recently, Shults and coworkers[17,18] have extended the theory of homogeneous-site glasses by accounting for the diffusion potential. For cases where either cations move in the glass by an interstitial mechanism ("solvated" ions), or cation transport is coupled with a counter-transport of negative vacancies, a description analogous to the Sandblom–Eisenman–Walker theory[25] of liquid ion-exchange membranes is obtained. This demonstrates the parallels between the second variant theory of Nikolskii and Shults and the usual concepts of liquid membranes.

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* The Chemical Abstracts transliteration gives Nikolskii and Shults, the forms used in the text of this paper (Ed.).

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ERPROBUNG UND VERGLEICH VON AUFSCHLUSSVERFAHREN ZUR SPURENANALYSE IN ERDÖLPRODUKTEN AN DEN BEISPIELEN CALCIUM, VANADIUM UND ZINK

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Zusammenfassung—Für die Spurenbestimmung des Ca, V und Zn-Anteils in Erdölprodukten mit der AAS wurden fünf vorgeschaltete Aufschlußmethoden (Trockenveraschung, Naßveraschung, Schöniger-Verbrennung, Kaltveraschung, und Veraschung unter Druckeinwirkung im Teflon-Zylinder) erprobt. Die Ergebnisse werden mit denen der direkten AAS (Lösungsmittel Toluol/Eisessig im Verhältnis 7:3) verglichen. Der Vergleich ergibt, daß für Spurenbestimmungen die Veraschung im Teflon-Zylinder und die Direktanalyse vorteilhaft sind. Trockenveraschung, Naßveraschung, Schöniger-Verbrennung und Kaltveraschung liefern nur befriedigende Ergebnisse.

In der modernen Motortechnologie reichen die Eigenschaften eines reinen Kohlenwasserstoffgemisches für die Bedürfnisse und Beanspruchungen in der Praxis nicht aus. Erst der Zusatz von verschiedenen Additiven gibt dem Öl—oder dem Kraftstoff—Eigenschaften, den Anforderungen gerecht zu werden. Metallhaltige Additive—Organometall- oder Komplexverbindungen—wirken zum Beispiel als Antiklopfmittel (Pb, Mn, Fe), Rückstandsumwandler (Ca, Ba, Mg), Metalldesaktivatoren, Antioxidantien und als Korrosionsinhibitoren (Ca, Zn).

Die Abmagerung und der erneute Zusatz der Additive kann über den Metallgehalt verfolgt und überwacht werden. Die Analyse des Schmieröls auf ihren Metallgehalt kann auch helfen, Schäden im Motor rechtzeitig zu erkennen und zu lokalisieren.[1] Im Folgenden wird über Analysenmöglichkeiten von Calcium, Vanadium und Zink in Gebraucht- und Frischölen berichtet. Das Vanadium stammt aus dem Erdöl und ist für viele Korrosionserscheinungen verantwortlich. Die simultane Bestimmung des Vanadiums erfolgt auch, weil für die Dosierung von Ca- und Zn-Additiven die Kenntnis des Vanadiumgehaltes erforderlich ist. Vanadate bilden mit Calcium- oder Zink Ablagerungen auf Motorteilen, die gegen korrosive Angriffe von sauren Bestandteilen des Motoröls schützen sollen.[2]

In der Routineanalytik hat sich die Atom-Absorptions-Spektrometrie (AAS) als einfache, schnelle Methode zur Bestimmung von Metallen in Erdölprodukten eingebürgert. Jedoch treten bei der direkten Analyse mit der AAS Störungen—besonders bei gebrauchten Ölprodukten—auf. Diese werden hervorgerufen durch große Abriebpartikel und Schmutzteilchen, die beim Atomisierungsprozeß nicht erfaßt werden. Außerdem gestaltet sich die Eichung des Analysenverfahrens schwierig, falls unterschiedliche Bindungsverhältnisse in Analysenprobe und Eichstandard vorliegen, was meist der Fall ist.[3] Auch muß zur Erreichung einer gleichen Sprührate der Eichstandard der Analysenprobe in Viskosität, Dichte und Säuregehalt angeglichen werden, da sonst Fehler bis zu 40% auftreten können.[4,5]

Gebrauchte Schmierölprodukte entwickeln während ihrer thermischen Zersetzung häufig soviel Rauch, daß die unspezifischen Lichtverluste nicht mehr mit dem Deuterium-Untergrundkompensator ausgeglichen werden können.

Um diese Schwierigkeiten zu unterdrücken und nach Möglichkeit ein brauchbares Referenzverfahren zu finden, wurden verschiedene Aufschlußverfahren getestet, damit für die AAS-Messung eine homogene wäßrige Lösung vorlag. Die Aufschlußverfahren[6] wurden den Gegebenenheiten der Spurenanalyse[7] angepaßt, optimiert und untereinander sowie mit der Direktmessung nach verschiedenen Gesichtspunkten wie Genauigkeit, Vollständigkeit des Aufschlusses, Streubreite der Ergebnisse usw. verglichen.

EXPERIMENTELLER TEIL

Geräte

Die Bestimmung des Metallgehaltes in Erdölprodukten erfolgte mit Atomabsorptions-Spektrometern der Firma Perkin–Elmer, und zwar mit den Geräten

300 S mit Flammen als Absorptionsvolumen

400 mit der Graphitrohrküvette HGA 72 (z.T. zusätzlich für V).

Schreiber: Hitachi Perkin–Elmer 56. Zur Anregung des Sauerstoffes durch Mikrowellen wurde ein Gerät der Firma Erbe-Elektromedizin, Oxidator 500 A, benutzt.

Reagenzien

Wäßrige Lösungen zur Eichung

100 ppm Ca	(Fixanal aus $CaCl_2$)
1000 ppm V	(Fixanal aus V_2O_5)
1000 ppm Zn	(Fixanal aus $ZnCl_2$)

Meßbedingungen[8]

	Ca	V	Zn
Resonanzlinie, *nm*	422.6	318.4	213.8
Spektrale Bandbreite, *nm*	0.7	0.7	0.7
Lichtquelle	HKL	HKL	HKL
Atomisierungsart	N_2O/C_2H_2	z.T.HGA 72 N_2O/C_2H_2	C_2H_2/Luft
Brennerart	3-Schlitz	3-Schlitz	3-Schlitz
Meßbereich, *ppm*	1–7	0.4–1(HGA) 20–100	0.4–1

Öllösliche Verbindungen zur Eichung

Ca:2-Ethylhexansäure Calciumsalz $C_{16}H_{30}CaO_4$.
V:Fixanal organo-Vanadium.
Zn:Cyclohexanbuttersäure, Zinksalz $C_{20}H_{34}ZnO_4$.
ASTM-1-Öl, zur Viskositätsregulierung der Eichproben, frei von anorganischen Bestandteilen.

Die pulverförmigen Eichstandards für Calcium und für Zink lösten sich schwer oder nur sehr langsam im Öl, so daß folgender Umweg beschritten wurde, um die vollständige Löslichkeit im Öl zu gewährleisten.

Eine entsprechende Menge an Calcium oder Zink-Salz wurde sorgfältig eingewogen und mit 20 ml Butanol-1 unter Schütteln homogenisiert und mit einem Lösungsmittelgemisch aus Toluol–Eisessig 70:30 bis zur Eichmarke aufgefüllt. Durch entsprechendes Verdünnen wurden die Eichlösungen auf einen optimalen Konzentrationsbereich gebracht.[8] Sie wurden zur Messung stets frisch angesetzt und den Probelösungen in Säurekonzentration, Dichte und Viskosität angepaßt, um eine gleiche Sprührate von Probe und Standard zu gewährleisten.

Lösungen für die Aufschlußverfahren

Veraschungshilfe: 10 g $Mg(NO_3)_2$ in 100 ml Ethanol
Ionisationsinhibitor: 2 g $SrCl_2$ in 100 ml DMSO
Übrige Reagenzien p.A., jeweils für sich auf Calcium, Vanadium und Zink analysiert.

Auswahl der Motoröle

Es wurden zwei Sorten Öl untersucht, und zwar:
(*a*) ein Gebrauchtöl, das *ca.* 70 Stunden in einem Versuchsmotor beansprucht wurde, sehr viskos war und Schmutzteilchen sowie Abriebpartikel enthielt;
(*b*) ein Frischöl, das nach Angaben des Herstellers frei von Vanadium und Calcium sein sollte. Über den Zinkgehalt lagen keine Angaben vor.

Grundsätzlich wurde vorher eine fünfstündige Homogenisierung der Ölprobe auf einer Schüttelmaschine durchgeführt, um eine einwandfreie Entnahme einer Durchschnittsprobe zu gewährleisten, da sich bei längerer Aufbewahrungszeit, insbesondere bei gebrauchtem Öl, infolge Sedimentation von Metallpartikeln lokale Konzentrationsprofile ausbilden können.[9]

Auswahl und Durchführung der Aufschlußverfahren

Folgende Aufschlußverfahren wurden für die Spurenanalyse von Metallen in Erdölprodukten erprobt.

Vorgeschaltete Aufschlüsse
1 Trockenveraschung
2 Naßveraschung
3 Veraschung in Sauerstoff, sogenannte "Schöniger Verbrennung"
4 Veraschung im Sauerstoffplasma, sogenannte "Kaltveraschung"
5 Veraschung unter Druck in der Polytetrafluorethylen (PTFE)-Bombe

Direktaufschluß durch thermische Zersetzung
6 In der Flamme

Die Durchführung der Aufschlußverfahren entsprach den üblichen Normen[6] der Spurenanalyse. In jedem Falle war es das Ziel, Verflüchtigungen auszuschalten, ein günstiges Verhältnis von Gefäßoberfläche zu Spurenelementmenge zu erreichen, in sauberer Atmosphäre zu arbeiten und nur kleinste Mengen leicht zu reinigender Aufschlußreagenzien zu verwenden.[7]

Die spezifischen Versuchsparameter der Aufschlußverfahren sind in Tabelle 1 aufgeführt. Eine Änderung der Arbeitsvorschriften aus der Literatur war zum Teil notwendig, um die Verfahren für die Spurenanalyse zu optimieren. Die Lösungen wurden nach den verschiedenen Aufschlußverfahren jeweils in geeigneter—für Frisch- und Gebrauchtöl, in gleicher—Weise verdünnt, um für die AAS-Bestimmung in günstigen Konzentrationsbereichen zu liegen, im oberen für das Gebrauchtöl, im unteren für das Frischöl.

Arbeitsvorschriften für die Aufschlußverfahren

Trockenveraschung. Ein g Öl in Platintiegel einwiegen, mit 5 ml Veraschungshilfe versetzen, bei 110° 3 h trocknen. 12 h über Nacht veraschen bei 425°, zweimal mit 2 ml konz. Salpetersäure abrauchen bis Asche weiß wird, dann mit 2 ml konz. Salzsäure aufnehmen.

Naßveraschung. Ein g Öl im Kjeldahl-Kolben mit 40 ml Säuregemisch (siehe Tabelle 1) tropfenweise vorsichtig versetzen, da sonst Nebelbildung; 12 h bei 160° veraschen, zur Vertreibung von nitrosen Gasen 15 ml Sulfanilsäure zugeben.

Schöniger Veraschung. Sauerstoff in Schöniger Kolben einleiten und 10 ml Absorptionslösung einpipettieren; 30 mg Öl auf ein Stück Filterpapier mit Anzündfahne geben, locker zusammenfalten und auf Platinnetz des Schöniger-Kolben-Schliffes (Abb. 1) stecken. Filterpapier anzünden und Schliffstopfen fest in Kolben drücken (Überdruck). Nach einer Absorptionsdauer von 15 min, Wasser in den Kragen des Kolbens füllen, Schliffstopfen lackern, Platinnetz mit 5 ml 1*N* Salzsäure sowie mit Wasser spülen.

Kaltveraschung. In Quartz-Schliffreagenzglas (Abb. 2) 100 mg Öl einwiegen, bei 5–8 mmHg Sauerstoff durch Mikrowellen anregen, im Plasma *ca.* 6 h veraschen, Aufschlußgefäß belüften, mit 1 ml konz. Salzsäure in Aufschlußapparatur rückflußkochen, und mit Wasser ausspülen.

Druck-Veraschung. Ein Hundert mg in Teflonzylinder (Abb. 3) einwiegen, 1 ml konz. Salpetersäure zugeben, Teflonbehälter in V_2A-Stahl Bombe verschließen, über Nacht bei 160° im Trockenschrank veraschen, auf Raumtemperatur abkühlen und mit Wasser in Meßkolben überführen.

Direktmessung in der Flamme. Ein g Öl in Meßkolben einwiegen, 2 ml Ionisationsinhibitor zugeben und mit Lösungsmittelgemisch Toluol/Eisessig auf Eichstrich auffüllen.

MESSERGEBNISSE

Die Meßergebnisse aus den AAS-Messungen (Flamme) gibt Tabelle 2 wieder. Sie wurden statistisch ausgewertet (Mittelwertbildung $\bar{x}$ und Standardabwei-

Tabelle 1. Spezifische Geräteparameter

	Trockenveraschung	Naßveraschung	Schöniger-Verbrennung	Kaltveraschung	PTFE-Druckveraschung	Direktaufschluß mit der AAS
Aufschlußgefäß	Platintiegel	Kjeldahl-Kolben	Schöniger-Kolben s. Abb.1	s. Abb.2	PTFE-Bombe s. Abb.3	AAS-Graphit-Rillenrohr oder Flamme
Aufschlußmedium	Therm. Zersetzung +5 ml Veraschungshilfe	Säuregemisch HNO_3: H_2SO_4:$HClO_4$ = 5:2:2	molekularer Sauerstoff + Absorptionsflüssigkeit	atomarer Sauerstoff durch Mikrowellenanregung	2 ml HNO_3 unter Druckeinwirkung	thermische Zersetzung
maximal aufzuschließende Ölmenge	10 g	10 g	30 mg	500 mg	100 mg	verschieden je nach Gehalt der Ölprobe
Temperatur	Temperaturgleitprogramm 100–450°C	130°C	Temperaturspitzen bis 1300°C	Temperaturspitzen bis 500°C	max. 157°C	Temperaturgleitprogramm
Aufschlußdauer	12 h ü. Nacht	12 h	10 min	4 h, je nach Ölsorte bzw. Menge	8 h ü Nacht	1 min
Besonderheiten	Simultanbestimmung der Asche möglich	vorsichtiges Arbeiten wegen Bildung explosiver Dämpfe	starker Blindwerteinfluß des Filterpapiers bei Ca	gleichzeitige Schwefelbestimmung im Öl möglich	bei zu hoher Einwaage "Abdampfer" durch Überdruck	Öl mit Toluol/Eisessig 70/30 verdünnt
Arbeitsweise	Asche mit 2 ml konz. HCl aufnehmen	langsame Zugabe der Säure, da starke Nebelbildung	Absorptionsflüssigkeit: 10 ml 1*N* HCl Abs. dauer: 15 min	O_2-Druck 4–6 mmHg	Aufschlußsäuremenge: 1 ml konz. HNO_3	
Literatur	11,12,26	13–15	16	17–19	20	6, 21–25

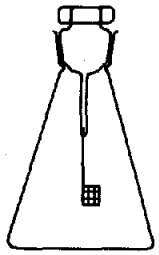

Abb. 1. Schöniger Kolben mit Platinnetz.[16]

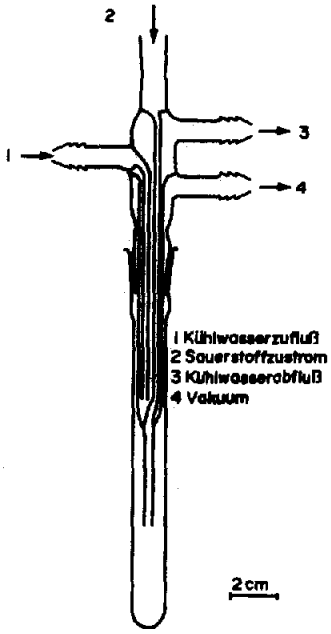

Abb. 2. Gefäß zur Kaltveraschung.[18]

chung s_G berechnet unter Eliminierung von signifikanten Fehlern und Ausreißern nach t-Test,[10] Zahl der Freiheitsgrade $n = 9$, statistische Sicherheit 95%). Kontrollmessungen mit Graphitrohrküvette bei Vanadium gaben keinen signifikanten Unterschied und wurden deshalb nicht gesondert aufgeführt. Die je 10 Aufschlüsse der gleichen Art wurden nach Möglichkeit gleichzeitig durchgeführt und die AAS-Messungen unmittelbar angeschlossen. Längere Standzeiten der Lösungen hatten eine Gehaltsverfälschung der Analysenergebnisse zur Folge. Wie aus Tabelle 2 zu ersehen ist, können die Ergebnisse bei den verschiedenen Aufschlußverfahren bis zum Faktor 3 voneinander abweichen. Aber kein Verfahren weist für alle drei Elemente Calcium, Vanadium und Zink einheitlich Maximal oder Minimalwerte auf, was bedeutet, daß kein Verfahren an sich unbrauchbar, aber möglicherweise für bestimmte Elemente besser oder schlechter ist. Calcium wurde im Frischöl—nach mehreren Verfahren—in deutlichen Mengen gefunden. Versuche mit dem ASTM-1-Öl gaben kein Signal für Calcium. Eine Calcium-Kontamination des Frischöles muß deshalb angenommen werden.

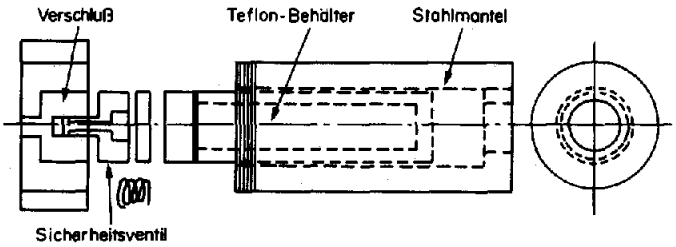

Abb. 3. PTFE-Bombe in V_2A-Stahl-Mantel (Eigenanfertigung).[20]

Tabelle 2. Meßergebnisse der Aufschlußverfahren

Aufschlußverfahren	statist. Funktion	Calcium Gebrauchtöl	Calcium Frischöl	Vanadium Gebrauchtöl	Vanadium Frischöl	Zink Gebrauchtöl	Zink Frischöl
Trockenveraschung	$\bar{x}$, *ppm*	312	46	1570	1	41	17
	s_G %	0,7	17	0,7	10	6	7
Naßveraschung	$\bar{x}$, *ppm*	294	14	1547	0	46	9
	s_G, %	0,6	22	3	—	4	10
Schöniger-Verbrennung	$\bar{x}$, ppm	568	137	547	0	20	14
	s_G, %.	10	28	1	—	8	10
Kaltveraschung	$\bar{x}$, *ppm*	514	0	1436	0	9	7
	s_G, %	4	—	3	—	19	27
PTFE-Veraschung	$\bar{x}$, *ppm*	365	57	1514	0	54	6
	s_G, %	5	3	11	—	9	14
Direktmessung in Toluol/Eisessig	$\bar{x}$, *ppm*	175	0	1425	0	36	5
	s_G, %	2	—	2	—	6	—

Tabelle 3. Beurteilung der Aufschlußverfahren

	Trockenveraschung	Naßveraschung	Schöniger-Verbrennung	Kaltveraschung	PTFE-Druck-veraschung	Direktmessung in Toluol/AcOH
Vollständigkeit	ja	ja	bis zu 30 mg	ja	ja	fraglich für Ca und Zn
Kontaminations-quellen	Laborluft	großes Auf-schlußmittel-volumen	Filterpapier	keine	siehe Zitat[7]	Lösungsmittel
zusätzliche auf-wendige Aufar-beitungsgänge	Abrauchen mit HNO_3, Auflösen der Asche in HCl	sorgfältiges Ausspülen der Aufschlußapparatur	intensive Spülung des Pt-Netzes	keine	keine	keine
Gefäßeinflüsse	gering	ja	starke	bei Zn	siehe Zitat[7]	keine
Anwendungsgrenzen	bei > 10 g	bei > 10 g	30 mg	Rußdämpfe bei > 100 mg	bei > 100 mg "Abdampfer"	Viskosität
Besonderheiten	Versuchstempe-ratur niedrig da sonst Verflüchtigung	stark saures System bewirkt Signalerniedrigung in der AAS	Pt-Netz nicht bei hohen Temperaturen zur Legierungs-bildung	gebrauchte Schmieröle besonders schwer zu veraschen	—	nicht brauch-bar für stark verschmutzte Schmieröle
Wirtschaftlichkeit Rentabilität	geringe Kosten einfache Arbeitsweise	personalintensiv in der Anfahrphase	geringe Investitionskosten, personalintensiv	hohe Investitions- und Unterhalts-kosten, perso-nalaufwendig	geringe Kosten, lange Aufschluß-dauer	schnelle Methode automatisierbar[1]
Beurteilung	befriedigend	befriedigend	ausreichend	befriedigend	gut	gut

DISKUSSION UND BEWERTUNG DER VERFAHREN

Die Suche nach systematischen Fehlern bei der Spurenanalyse in Bereichen kleiner als 10^{-3}% ist zeitraubend und mühselig, da oft Kombinationen—zusammengesetzt aus mehreren Fehlern—auftreten. Jedes Verfahren muß nach bestimmten Punkten hin untersucht werden, zum Beispiel auf:

Verflüchtigung;

Kontamination (Unsaubere Reagenzien, Vorgeschichte der Gefäßmaterialien, unsaubere Laboratoriumsluft);

Verluste durch Adsorption an der Oberfläche der Aufschlußapparatur;

Verluste durch zu viele Aufarbeitungsschritte.

Die folgenden systematischen Fehler ließen sich eindeutig zuordnen.

Calcium-Bestimmung nach Schöniger-Veraschung. Ergebnisse sind zu hoch durch Kontamination aus Kolben und Filterpapier. Wegen der geringen Einwaage macht sich eine kleine Kontamination stark bemerkbar. Ähnliches dürfte für die Kaltveraschung gelten.

Calcium-Bestimmung in Gebrauchtöl bei Direktmessung. Ergebnisse sind zu niedrig, da Kolloidteilchen nicht vollständig atomisiert werden.

Vanadium-Bestimmung nach Schöniger-Verbrennung. Ergebnisse sind zu niedrig. Salzsäure erwies sich als ungeeignet zur Absorption wegen starker Vanadium-Adsorption an Gefäßwand und Platinnetz. Speziell für Vanadium-Bestimmungen nach Schöniger-Aufschluß sollten Alkalilaugen als Absorptionsflüssigkeit verwendet werden. Alle anderen Vanadium-Meßwerte sind unabhängig vom Aufschlußverfahren überraschend homogen.

Zink-Bestimmung nach Kaltveraschung. Ergebnisse sind zu niedrig. Die Temperatur überschritt teilweise 730°, so daß Zink sowohl verflüchtigt als auch in das Quarzgitter des Gefäßes eingebaut werden konnte.

In allen anderen Fällen können für die Bestimmung der Einzelelemente keine konkreten Fehlerursachen angegeben werden. Zusätzlich wurde eine mehr qualitative und subjektive Bewertung der Aufschlußverfahren nach verschiedenen Kriterien vorgenommen, die in Tabelle 3 zusammengestellt sind.

Nach Abwägung aller Argumente kann man feststellen, daß die Veraschung unter Druckeinwirkung in der PTFE-Bombe im Hinblick auf die Forderung nach einer Präzisionsanalyse für alle drei Elemente als die Methode der Wahl für den Aufschluß von Erdölprodukten bezeichnet werden kann. Die Durchführung im Routinebetrieb und die einfache Durchführung halten die Kosten für eine Analyse niedrig. Systematische Fehler werden so klein wie möglich gehalten, da *Adsorptionseffekte* an der Oberfläche des PTFE-Werkstoffes kaum zu beobachten sind und *Kontaminationsquellen* weitestgehend ausgeschlossen werden (geschlossene Apparatur, geringe Menge an leicht zu reinigendem Aufschlußreagenz, geringe Mengen an Ausspülflüssigkeit). Über Störungen durch Diffusion von nitrosen Gasen durch den PTFE-Werkstoff nach mehrmaligem Gebrauch wird berichtet.[7]

Als Alternative zu diesem Verfahren kann die Direktanalyse in Toluol/Eisessig angesehen werden. Sie ist vor allem schnell. Grundsätzlich werden hier zu kleine Werte erhalten. Systematisch auftretende Abweichungen können leicht durch einen gesondert zu ermittelnden Korrekturfaktor ausgeglichen werden. Die sehr niedrigen Calcium-Werte sind aber sicher auf feste oder kolloid gelöste Anteile zurückzuführen, die nicht vollständig atomisiert werden. Für eine Präzisionsanalyse oder um Unterschiede im kolloiden Anteil mit zu erfassen ist deshalb ein Aufschluß unumgänglich.

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APPLICATION OF COMPETITIVE REACTION SYSTEMS TO CATALYTIC KINETIC ANALYSIS—DETERMINATION OF PHOSPHATE

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Summary—A technique is described for the determination of catalytically active substances, in which a slow catalysed reaction is coupled to a fast competitive reaction. One reactant, which at the same time serves as the indicator substance, is removed by the slow reaction as well as by the competitor added to the system from outside. Under suitable conditions the time for the complete removal of the indicator substance is dependent only on the rate of the catalysed reaction and consequently on the catalyst concentration. The technique is illustrated by means of the phosphate-catalysed reduction of Mo(VI) by ascorbic acid.

Kinetic measurements of reaction rates may be accomplished either in "closed" systems without any material change from the outside during the reaction or in "open" systems, where components are moved into and/or out of the system during the course of the reaction under study. Well-known examples of the latter technique are the "flow",[1] "steady-state",[2] and "stat" methods,[3] which are valuable tools in the analytical chemistry of catalytically active substances.

In this paper we investigate the method of competitive reactions, applied by Smith and Downing to the evaluation of rate constants,[4] with respect to its applicability in the field of analytical determination of catalyst concentrations. By the definition given above, this method belongs to the group of open systems.

In a system of two parallel reactions

(I) $A + B \xrightarrow{k_I} P_I$ (reaction under study)

and

(II) $B + R \xrightarrow{k_{II}} P_{II}$ ($k_{II} \gg k_I$)

one reactant (B) is consumed by the slow reaction (I) as well as by the fast competitive reaction (II). The competitor R reacts with B as fast as it is introduced into (or generated within) the system containing A and B. If the rate of addition (ρ_R = const.) is preset, then the time t_c (where c implies "competitive") required to remove all of B ($C_B = 0$) is dependent only on the rate of the slow reaction (I). The state $C_B = 0$ must be detectable, of course, with a suitable indicator system. Furthermore, any change in the volume of the reaction mixture by the addition of R has to be small, so that it can be neglected.

For the pseudo-first-order case with A present in great excess, the time t_c is given[4] by:

$$t_c = \frac{1}{k_I C_{0A}} \ln\left(\frac{k_I C_{0A} C_{0B}}{\rho_R} + 1\right) \quad (1)$$

where C_{0A} and C_{0B} are the initial concentrations of A and B. In the absence of A, B is removed only by reaction with R and t_c is then identical with the time t_R necessary for the complete titration of B with R.

$$t_R = \frac{C_{0B}}{\rho_R} \quad (2)$$

Dividing t_c by t_R leads to the equation

$$\frac{t_c}{t_R} = \frac{1}{Q} \ln (Q + 1) \quad (3)$$

where

$$Q = k_I C_{0A} C_{0B} / \rho_R .$$

It is obvious that only values ≤ 1 can be obtained for t_c/t_R. In this form the competitive reaction method was used by Smith and Downing[4] for the evaluation of rate constants k_I by using experimentally determined t_c/t_R-values.

We have extended this principle to the analytical determination of substances which are catalytically active in the slow reaction between A and B. Again assuming pseudo-first-order conditions, the rate of consumption of B in the catalysed system can be written as

$$-\frac{dC_B}{dt} = k_I' C_{Cat} C_{0A} C_B + \rho_R \quad (4)$$

where the catalyst concentration C_{Cat} = const. By this means the ratio Q in equation (3) is changed to

$$Q = \frac{k_I' C_{Cat} C_{0A} C_{0B}}{\rho_R} \quad (5)$$

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If in a series of experiments all parameters except C_{Cat} are held constant, then Q and consequently t_c are functions only of C_{Cat}:

$$Q = k''_1 C_{Cat} \qquad (6)$$

Thus, unknown concentrations C_{Cat} can be determined by measuring t_R and the different t_c values and using a t_c/t_R *vs.* C_{Cat} calibration graph.

We have chosen the phosphate-catalysed reaction between molybdate and ascorbic acid[5,6] as an example of the determination of catalyst concentrations by the technique mentioned above.

(III)

$$\text{Mo(VI)} + \text{ascorbic acid} \xrightarrow{H_2PO_4^-} \text{Mo(V)} + \text{dehydroascorbic acid}$$

This is the "slow branch" in a system of competitive reactions with Mo(VI) as reactant A which is present in great excess. Ascorbic acid is reactant B and orthophosphate the catalyst, the concentration of which (C_{Cat}) is to be determined. As a fast competitive reaction for B we chose

(IV)

$$I_2 + \text{ascorbic acid} \rightarrow 2\,I^- + \text{dehydroascorbic acid}$$

with iodine as the competitor R.

EXPERIMENTAL

Reagents

A 0.06*M* solution of Mo(VI) in dilute sulphuric acid is prepared by dissolving 1.451 g of $Na_2MoO_4 \cdot 2H_2O$ and making up to 100 ml with 0.6*M* sulphuric acid. The solution is allowed to stabilize for one day before use.

A stabilized 0.05*M* ascorbic acid solution is made by dissolving 0.881 g of L(+)-ascorbic acid and 0.05 g of EDTA in 100 ml of doubly distilled water. If stored in darkness, this solution is stable for two weeks.

A 0.01*M* I_2 solution is prepared daily from a 0.05*M* iodine stock solution.

Calibration measurements are performed with dilute orthophosphate solutions, made from a stable 100-ppM P stock solution (0.4393 g of KH_2PO_4 in 1 litre of doubly distilled water) (ppM = parts per milliard).

Procedure

The apparatus for the measurement of the time t_c and t_R is basically the same as that used in iodometric titrations. It consists of a motor-driven burette which delivers the 0.01*M* iodine solution at a constant rate and a potentiometric or a biamperometric end-point detector. In a 20-ml polyethylene beaker 1 ml of the Mo(VI) solution is added to 5 ml of the sample solution containing 0–1.2 ppM of P (in the form of orthophosphate). A platinum indicator electrode and an SCE reference electrode are inserted into the vessel. The capillary tip of the burette is immersed in such a way that with rapid magnetic stirring the stream of iodine delivered does not directly reach the electrodes. The catalysed reaction is initiated by adding 10 μl of the stabilized ascorbic acid with a microlitre pipette, and at the same time the motor-driven burette (delivery rate 10 μl/min) is started. The start is marked on a strip-chart recorder which monitors the potential difference between the two electrodes. After a few minutes a potential jump is observed (see Fig. 1), indicating the existence of free iodine in the solution and the complete consumption of the ascorbic acid. The time t_c may be obtained graphically from the recorder graph as shown in Fig. 1. Alternatively the state $C_B = C_{asc.ac.} = 0$ can be indicated biamperometrically, by using two platinum electrodes and applying a polarization voltage of 60 mV. The titration graphs obtained exhibit a sharp "end-point" (see Fig. 2). After each measurement the beaker and electrodes are rinsed with 0.05*M* sulphuric acid and then with doubly distilled water.

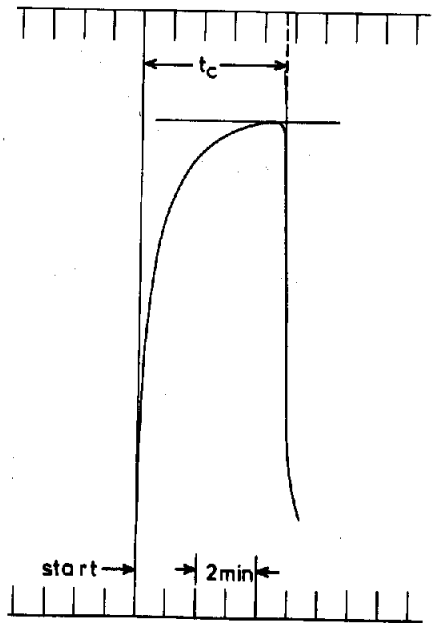

Fig. 1. "Titration" curve for 0.4 ppM P and graphical evaluation of t_c. Potentiometric detection.

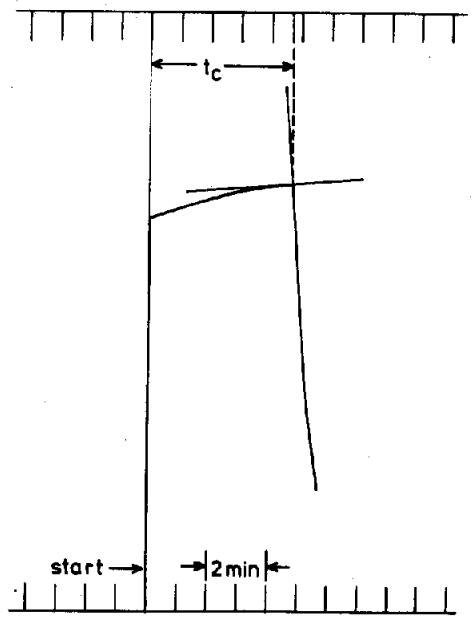

Fig. 2. "Titration" curve for 0.4 ppM P and graphical evaluation of t_c. Biamperometric detection.

For each series of measurements the value t_R has to be determined. This can easily be done by simply using distilled water instead of the phosphate solution. In this case ascorbic acid is used up almost exclusively by iodine because the uncatalysed reaction between ascorbic acid and Mo(VI) can be neglected at the chosen pH value (pH ≈ 0.7).

The measured times are converted into the dimensionless form t_c/t_R. Unknown phosphate concentrations can be derived from the measured t_c values by means of a t_c/t_R *vs.* catalyst concentration calibration plot (0.0–1.2 ppM P).

RESULTS AND DISCUSSION

The experimental conditions for the Mo(VI)/ascorbic acid reaction have been optimized, including the suggestions given by Crouch and Malmstadt.[5]

In order to find a suitable working range for phosphate determinations, a plot of t_c/t_R *vs.* phosphate concentration up to 20 ppM P was prepared from experimental data. The curve in Fig. 3 represents a graphical verification of equation (3) (with $Q = k_1'' C_{Cat}$). Starting with $C_{Cat} = 0$ and $t_c/t_R = 1$ an increasing catalyst concentration results in an increasing consumption of ascorbic acid by reaction (IV). Therefore, at a constant addition rate ρ_R of the iodine, the time t_c and also the ratio t_c/t_R will decrease with increasing catalyst concentration. As can be seen from Fig. 3, a nearly linear and sufficiently steep slope of the calibration curve can only be expected in the range below 2 ppM P.

A calibration graph in the range 0.0–1.2 ppM P was prepared. The regression line, derived from the statistical treatment of 35 measurements, follows the equation

$$t_c/t_R = (0.997 \pm 0.010) - (0.263 \pm 0.018)C_p$$

at the 99% confidence level.

The proposed method has the advantage that it is not necessary to run standards together with each series of samples as is usual in kinetic analysis. Any possible small change in concentration of the ascorbic acid or of the iodine solution shifts the t_c values in the same direction as t_R, so that the ratio t_c/t_R only varies within the confidence interval. Therefore only t_R has to be measured together with the samples.

The temperature-dependence of the system has been investigated between 20 and 30°. No significant change in the t_c/t_R values could be observed. Under normal laboratory conditions temperature-control of the reaction system therefore does not seem to be necessary.

The influence of several anions and cations was investigated with the idea of a practical application of the method in mind. Sample solutions of 0.5 ppM P containing up to tenfold concentration of the ion under study were prepared and analysed according to the procedure given above. The results are listed in Table 1. As can be expected, severe interferences derive from strong oxidants such as chromate, nitrite and iron(III), and from strong reductants such as sulphide and sulphite. The interference by Fe(III) can be overcome by the addition of EDTA. As with phosphate, silicate is also able to produce a heteropoly acid with Mo(VI) and to catalyse the reduction of Mo(VI) by ascorbic acid. The interference is negligible up to a 20-fold amount of silicate with respect to phosphate. This limit can be increased by the addition of citric or tartaric acid.[7] Both reagents prevent the formation of molybdosilicic acid but may also influence the phosphate-catalysed reaction when present in a large excess.

The "titration" technique described should also be applicable to other catalysed reactions. Preliminary investigations have shown, for example, that the reaction between iodine and azide can be combined with the fast competitive reaction between iodine and ascorbic acid:

$$2N_3^- + I_2 \xrightarrow{Cat} 3N_2 + 2I^-$$

$$I_2 + \text{ascorbic acid} \rightarrow 2I^- + \text{dehydroascorbic acid}$$

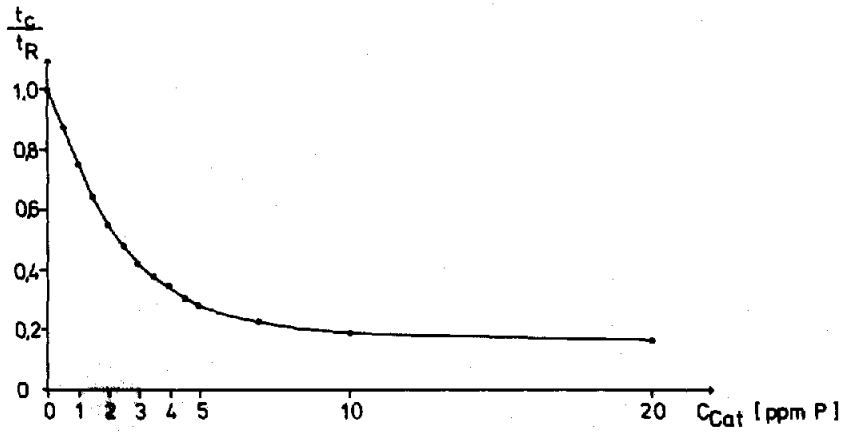

Fig. 3. Dependence of t_c/t_R on the phosphate concentration.

Table 1. Interference studies at a concentration of $[H_2PO_4^-] = 1.6 \times 10^{-5} M = 0.5$ ppM P

Ion under study	[interfering ion]:$[H_2PO_4^-]$			
	10:1	1:1	1:2	1:5
F^-	0	0	0	0
Cl^-	0	0	0	0
NO_2^-	+	+	+	0
S^{2-}	+	+	+	0
SO_3^{2-}	+	+	+	0
$Cr_2O_7^{2-}$	+	+	+	+
SiO_3^{2-}	0	0	0	0
AsO_4^{3-}	0	0	0	0
Ca^{2+}	0	0	0	0
Mg^{2+}	0	0	0	0
Pb^{2+}	0	0	0	0
Mn^{2+}	0	0	0	0
Fe^{3+}	+	+	0	0
Cu^{2+}	0	0	0	0

+ means interference: t_c/t_R outside the confidence interval.
0 means no interference.

In this case ascorbic acid is the competitor. The system can be applied to the determination of catalysts containing bivalent sulphur, *e.g.*, sulphide, thiosulphate and cystine. Most of these substances, however, are depleted by oxidation in a side-reaction with iodine. Therefore a modified version of coupling competitive reactions is under study, in which the sulphur-containing catalyst is maintained in a reducing medium during the measurement. This will be reported elsewhere.

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UNTERSUCHUNGEN ZUR ATOMSPEKTROSKOPISCHEN SPURENANALYSE IN $A^{III}B^{V}$-HALBLEITER-MIKROPROBEN—IV*

VERGLEICH DER BESTIMMUNG VON TELLURSPUREN IM GaP UND GaAs DURCH AAS, AFS UND AES

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Zusammenfassung—Es werden atomspektroskopische Methoden für die Bestimmung von Te-Spuren in saurer Lösung in Gegenwart und Abwesenheit der anorganischen Matrices As, Ga, P, GaP und GaAs und in GaP- bzw. GaAs-Feststoffen beschrieben. Als Methoden wurden eingesetzt: AAS mit elektrothermischer Atomisierung, AFS mit elektrothermischer Atomisierung und AES mit Gleichstromdauerbogenanregung. Die Bedingungen der Methoden wurden optimiert und die Resultate miteinander verglichen. Es wird gezeigt, daß die AAS mit elektrothermischer Atomisierung die besten absoluten und auch relativen Nachweisgrenzen für Te-Spuren liefert (90 pg Te, 4 ppm Te in GaAs oder GaP). Deshalb wird diese Methode für die Bestimmung von Te-Spuren in $A^{III}B^{V}$-Halbleiter-Mikroproben empfohlen.

Tellur wird als Dotierungselement für $A^{III}B^{V}$-Halbleiter zur Erzielung von *n*-Leitung und von bestimmten optoelektronischen Eigenschaften eingesetzt. Eine analytische Kontrolle des Tellurgehaltes ist erforderlich. In Abhängigkeit vom Herstellungsverfahren des Te-dotierten Materials kann sich dabei sowohl das Problem der Spurenanalyse im Mikrobereich (Probemenge < 1 mg) als auch im Halbmikrobereich (Probemenge 10—100 mg) ergeben.

Für die Lösung dieser Aufgabenstellung sollten nachweisstarke atomspektroskopische Bestimmungsmethoden eingesetzt werden: 1. AAS mit elektrothermischer Verdampfung, 2. AFS mit elektrothermischer Verdampfung und 3. AES mit Gleichstromdauerbogenanregung. Eine Betrachtung der Möglichkeiten, die sich bei Anwendung der Hydridtechnik für die gegebene Aufgabenstellung ergeben, erfolgt in der Mitteilung V.

In den vergangenen Jahren sind einige Mitteilungen über die Bestimmung von Tellurspuren mit Hilfe atomspektroskopischer Analysenmethoden veröffentlicht worden. Der Einsatz der AAS mit elektrothermischer Verdampfung führte zu absoluten Nachweisgrenzen im Pikogrammbereich.[1–7] Ähnliche Nachweisgrenzen wurden auch mit der flammenlosen AFS erzielt.[8,9] Eine vollständige Bewertung der bisher beschriebenen AES-Methoden ist an dieser Stelle nicht möglich. Es wurde i.a. versucht, das gegenüber der AAS und AFS geringere absolute Nachweisvermögen durch Anreicherungsverfahren zu verbessern.[10–13]

In fast allen Veröffentlichungen wird auf Störungen durch die Matrix eingangen. So berichtet Sverdlina,[3] daß die Tellurbestimmung im GaAs durch AAS bereits bei einer Matrixkonzentration von 0,01 mg Ga/ml gestört wird. Laszkiewicz[13] und Nasarenko[14] umgehen entsprechende Effekte durch Anwendung einer chemischen Spur–Matrix-Trennung durch Extraktion mit nachfolgender Bestimmung durch AES bzw. AAS.

Da für die Lösung spurenanalytischer Problemstellungen im Mikrobereich Anreicherungen nicht möglich sind und vorherige chemische Trennungen die Gefahr der Kontamination mit sich bringen, sollten in dieser Arbeit die Möglichkeiten der Tellurspurenbestimmung in Gegenwart anorganischer Matrices bei Einsatz der erwähnten nachweisstarken atomspektroskopischen Bestimmungsmethoden ermittelt werden. Durch Vergleich der analytischen Resultate, die bei der Lösung dieses konkreten analytischen Problems erhalten werden, sollte eine Aussage über die Leistungsfähigkeit der genannten Methoden gemacht und eine optimale Variante angegeben werden.

EXPERIMENTELLER TEIL

Apparatives

AAS:

Spektrometer: Zweikanal-AAS-Gerät, Typ 811, Jarrell-Ash, USA.

Atomisator: Graphitrohrküvette Typ 1268, Beckman, USA.

Lichtquelle: Te-HKL, Jarrell-Ash, USA, 5 mA, spektrale Bandbreite: 0,2 nm, λ = 214,3 nm. Die Untergrundkompensation erfolgte nach der Zweilinienmethode: Sn-HKL, Jarrell-Ash, USA, 5 mA, spektrale Bandbreite: 0,4 nm, λ = 215,3 nm.

AFS:

Spektrometer: Einkanal-AF-Spektrometer, Eigenbau.[15,16]

Atomisator: Graphitstabatomisator, Eigenbau.[17]

Lichtquelle: Te-EDL, Eigenbau, λ = 214,3 nm. Anregung: Mikrowellengenerator mit Spektroskopiekonzentrator (3/4 λ-Küvette), Bosch, BRD; maximale Spaltbreite des Monochromators: 3 mm.

* Mitteilung III: *Talanta*, 1978, **25**, 243.

AES:
Spektrograph: Plangitterspektrograph PGS 2, Zeiss, DDR. Gitter 651 Strich/mm, Blaze-λ: 300 nm, 1. Ordnung. Plattenmitte: 238 nm, Spaltbreite: 0,02 mm.
Anregung: Universalbogenimpulsgenerator UBI 1, Zeiss, DDR. Gleichstromdauerbogen 6 und 15 A. Feststoffanalyse: anodische Verdampfung, 6 A. Lösungsanalyse: kathodische und anodische Verdampfung, 15 A.
Elektroden: Graphitelektroden, Durchmesser: 5 mm. Feststoffanalyse: Anode–Becherform; Kathode–stumpfer Kegel. Lösungsanalyse: Anode = Kathode, oberer Randdurchmesser: 3,5 mm.
Registrierung: Photoplatten ORWO WU 3 und ORWO UV 1, Filmfabrik Wolfen, DDR.
Auswertung: Te I 238,5 nm als Analysenlinie. Bi I 240,0 nm als Linie des inneren Standards.

Elementkonstanten

Tellur: Ionisierungspotential: 8,96 eV; Siedepunkt: 990°. Grundzustand: $5p^4\ ^3P_2$
Übergang bei 214,3 nm: $5p^4\ ^3P_2 \rightarrow 6s\ ^3S_1$ (E_a = 5,83 eV)
Übergang bei 238,5 nm: $5p^4\ ^3F_1$ (E_a = 0,59 eV) $\rightarrow 6s\ ^3S_1$.

Lösungen

Durch oxydatives Lösen von reinem Tellur in konzentrierten Säuren, nachfolgendes Eindampfen und Aufnehmen in 1*M* Salzsäure oder 1*M* Salpetersäure wurden die Stammlösungen gewonnen, die 1 mg Te pro ml enthielten.[3] Die erforderlichen Matrixlösungen (Ga^{3+}; PO_4^{3-}; AsO_4^{3-}) wurden, wie in Mitteilung II[18] beschrieben, hergestellt (Matrixelement 200 mg/ml). Durch entsprechendes Mischen konnten die beim oxydativen Lösen von GaAs und GaP entstehenden Lösungen hergestellt und somit diese Matrices simuliert werden.

Feststoffe

Für die Feststoffanalyse durch AES wurden jeweils 5 mg festes GaP oder GaAs eingesetzt. Diese Substanzen wurden für die Analyse im Verhältnis 1:3 mit Kohlepulver gemischt. Das Kohlepulver enthielt als inneren Standard 1% Bi_2O_3. Die Dotierung des Tellurs erfolgte sowohl direkt als auch in Form von TeO_2.

Allgemeine Arbeitsweise

Für die AAS und AFS-Untersuchungen wurden Lösungsvolumina von 0,01 ml, die die Spuren und Matrices in entsprechenden Konzentrationen enthielten, in die Graphitrohrküvette (GRK) bzw. auf den Graphitstabatomisator (GSA) gegeben, verascht und atomisiert. Für die AES-Feststoffanalyse wurden jeweils 20 mg des Probe–Kohlepulver-Gemisches in die Becherelektrode gestopft und der Gleichstrombogenanregung ausgesetzt.

Für die AES-Lösungsanalyse wurden jeweils 0,025 ml auf beide Graphitelektroden gegeben, so daß die Gesamtmatrixmenge 5 mg war. Die Lösungen wurden durch IR-Strahlung getrocknet. Die Rückstände wurden der Gleichstrombogenanregung ausgesetzt.

RESULTATE UND DISKUSSION

Untersuchungen zur Atomabsorptionsspektrometrie (AAS) mit elektrothermischer Verdampfung

Zur Ermittlung des optimalen Mediums wurden Tellurhaltige 1*M* salz- bzw. salpetersaure Lösungen getestet. In Übereinstimmung mit Tölg[4] wurde die beste Empfindlichkeit für die Te-AA in 1*M* Salpetersäure erzielt. Wie aus der Abb. 1 hervorgeht, trat jedoch in Gegenwart von 1*M* Salpetersäure eine unspezifische, nicht kompensierbare Absorption auf. Trotz Steigerung der Veraschungstemperatur auf den maximal möglichen Wert von 1200° konnte dieser Blindwert nicht vollständig beseitigt werden. Die Ursache dieses Blindwertes konnte nicht exakt geklärt werden (vgl. Mitteilung I[19]).

Bei Verwendung von 1*M* Salzsäure sank die Empfindlichkeit gegenüber 1*M* Salpetersäure auf 75%. Da jedoch der unspezifische Blindwert vollständig vermieden wurde, wurde dieses Medium für die weiteren Untersuchungen ausgewählt. Das erzielte Nachweisvermögen (90 pg Te) ist mit den Literaturwerten vergleichbar (vgl. Tab. 1).

Ausführliche Untersuchungen wurden sowohl zur Ermittlung des Einflusses der Einzel- wie auch der komplex zusammengesetzten Matrices durchgeführt. Es wurde festgestellt, daß Tellur nach dem Arsen verdampft und daß infolge dieser thermischen Matrix–Spur-Trennung Te-Bestimmungen in Gegenwart von 0,1 mg Arsen pro 0,01 ml ohne Einschränkung möglich sind. Eine ähnliche Spur–Matrix- oder Matrix–Spur-Trennung konnte in Gegenwart von Phosphor (als PO_4^{3-}) nicht erzielt werden. Beide Substanzen verdampfen gleichzeitig. Die Untergrundkompensation ermöglicht eine Bestimmung des Tellurs in Gegenwart von 0,03 mg Phosphor pro 0,01 ml. Auch in Gegenwart von Ga^{3+}-ionen und den komplex zusammengesetzten Matrices (Ga^{3+}/PO_4^{3-} bzw. Ga^{3+}/AsO_4^{3-}) treten depressive Effekte und in Abhängigkeit von der Matrixkonzentration nicht kompensierbare Blindwerte auf. Eine thermische Abtrennung des Tellurs war nicht möglich, so daß analytische Te-Bestimmungen nur in Gegenwart von 0,05 mg GaP bzw. GaAs pro 0,01 ml möglich waren. Die analytischen Resultate sind in der Tabelle 1 (Zeile 1–6) zusammengefaßt worden.

Zum Zweck des exakten Vergleiches der AAS-Resultate mit denen der AFS wurden auch AAS-Untersuchungen bei Verwendung des GSA durchgeführt. Die Resultate für 1*M* salzsaure Tellurat-Lösungen sind in der Zeile 7 der Tabelle 1 enthalten. Ein Vergleich zwischen Zeile 1 und 7 zeigt, daß die mit dem GSA erhaltenen Nachweisgrenzen etwa eine Größenordnung schlechter sind. Das ist auf die ungünstigeren thermischen Verhältnisse dieses Atomisators zurückzuführen. Von der Oberfläche des Gra-

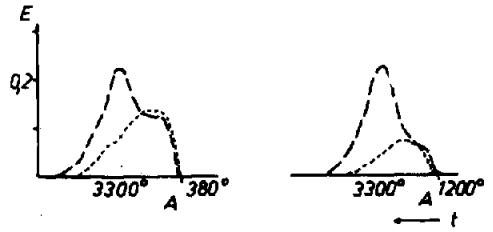

Abb. 1. Extinktions–Zeit-Kurven für die AA-Bestimmung von Tellur in 1*M* Salpetersäure bei Verdampfung in einer Graphitrohrküvette. Bedingungen: Untergrundkompensation mit der Zweilinienmethode 214,3/215,3 nm. A: Atomisierungsbeginn, Schreibergeschwindigkeit: 600 mm/min. —— 1 ng Te (als TeO_4^{2-}) in 1*M* HNO_3. --- 1*M* HNO_3.

Tabelle 1. Analytische Ergebnisse der Te-Spurenbestimmung durch AAS und AFS mit elektrothermischer Verdampfung und AES mit Gleichstromdauerbogenanregung in Gegenwart und Abwesenheit von anorganischen Matrices

No.	Methode	Atomisator bzw. Photoplatte	Matrix, μg*	Nachweisgrenzen (3s) absolut, ng	relativ, ppm	relativ, At/cm^3	linearer Konzentrationsber., ng	Reziproke† Empfindlichkeit, ng
1	AAS	GRK	1*M* HCl	0,09	0,009	—	2	0,04
2	AAS	GRK	As 100	0,09	0,9	—	2	0,04
3	AAS	GRK	P 30	0,4	13	—	5	0,14
4	AAS	GRK	Ga 100	0,6	6	—	5	0,16
5	AAS	GRK	GaP 50	0,22	4,4	$8{,}6 \times 10^{16}$	5	0,08
6	AAS	GRK	GaAs 50	0,17	3,4	$8{,}5 \times 10^{16}$	5	0,09
7	AAS	GSA	1*M* HCl	1,1	0,11	—	10	0,9
8	AFS	GSA	1*M* HCl	0,5	0,05	—	30	0,5
9	AFS	GSA	P 10	4	400	—	25	1,7
10	AFS	GSA	Ga 100	5	50	—	25	1,7
11	AFS	GSA	GaP 50	1,9	18	$3{,}5 \times 10^{17}$	300	1,7
12	AES Feststr.	UV 1	GaP 5000	110	23	4.5×10^{17}	50000	—
13	AES Feststr.	WU 3	GaP 5000	340	70	$1{,}3 \times 10^{18}$	50000	—
14	AES Lösung	UV 1	GaP 5000	250	50	$1{,}0 \times 10^{18}$	50000	—

* AAS und AFS: jeweils maximal mögliche Matrixmenge pro 0,01 ml. AES: eingesetzte Matrixmenge.
† AAS: RE bezogen auf den Extinktionswert 0,01. AFS: RE bezogen auf kleinste auswertbare Peakfläche.

phitstabes zum Untersuchungsraum hin bewirkt der stark negative Temperaturgradient auf Grund von Molekülbildung und auch Kondensation eine Verminderung der Te-Atomkonzentration. Untersuchungen in Gegenwart von Matrices wurden aus diesen Gründen nicht durchgeführt.

Untersuchungen zur Atomfluoreszenzspektrometrie (AFS) mit elektrothermischer Verdampfung

Die Resonanzfluoreszenz bei 214,3 nm ergab die höchste Intensität, so daß bei dieser Wellenlänge gearbeitet wurde. Es wurde der Lösungsmitteleinfluß von Wasser, 1*M* Salzsäure und 1*M* Salpetersäure untersucht und festgestellt, daß keine Unterschiede der Te-AF auftraten. Die in 1*M* Salzsäure erzielte absolute Nachweisgrenze liegt mit 500 pg etwas schlechter als die besten in der Literatur beschriebenen Resultate. Dies ist vor allem auf die in diesem Wellenlängengebiet verminderte Lichtstärke des im AF-Spektrometer verwendeten Prismenmonochromators (SPM 1, Zeiss, DDR) zurückzuführen.

Ein Vergleich mit den Resultaten der AAS bei Verwendung des gleichen Atomisators (Zeile 8 mit 7, Tab. 1) zeigt, daß die absolute Nachweisgrenze bei Einsatz der AFS um den Faktor 2 besser ist. Dieses Resultat bestätigt, daß mit Hilfe der AFS auch mit relativ einfachen Mitteln bei der Untersuchung reiner Lösungen sehr gute analytische Ergebnisse erzielt werden können. Vergleicht man die mit der AFS erzielten Werte jedoch mit den besten AA-Werten, die bei Einsatz der Graphitrohrküvette erhalten, wurden, so sind die der AAS um den Faktor 5 besser (Zeile 8 mit 1 der Tabelle 1). Für die praktische Analytik ist demnach die AAS vorzuziehen.

Diese Einschätzung wurde auch bestätigt bei der Untersuchung der Einflüsse der Matrices Ga^{3+}, PO_4^{3-} und Ga^{3+}/PO_4^{3-} jeweils im 1*M* salzsauren Medium. Es konnte gezeigt werden, daß Bestimmungen des Tellurs durch AFS in Gegenwart dieser Matrices prinzipiell möglich sind. Wie aus der Betrachtung vergleichbarer Werte (Zeile 9 mit 3; 10 mit 4 und 11 mit 5) hervorgeht, sind jedoch die depressiven Einflüsse dieser Matrices nicht kleiner als bei der AAS. Besonders bemerkbar macht sich auch der stark zunehmende Streulichtanteil, der infolge der schnellen Kondensation der anorganischen Matrices im thermisch heterogenen Plasma des GSA stark anwächst. Somit konnten bei Einsatz der AFS für die Te-Bestimmungen in Gegenwart der getesteten Matrices auch keine gegenüber der AAS verbesserten, relativen Nachweisgrenzen erhalten werden.

Wie aus der Tabelle 1 hervorgeht, ergibt sich jedoch für die AFS gegenüber der AAS der Vorteil des bedeutend größeren auswertbaren Konzentrationsbereichs. Aus diesen Resultaten ist abzuleiten, daß auch bei Einsatz von lichtstärkeren Monochromatoren oder intensiveren Anregungsquellen keine besseren analytischen Ergebnisse zu erwarten sind, da sich die Hauptquelle der Störungen, der Streulichtanteil, damit nicht reduzieren läßt. Eine Möglichkeit besteht bei Anwendung der Direktlinienfluoreszenz in Verbindung mit einer teilweisen Ausblendung der dann störenden Strahlung der Lichtquelle. Entsprechende Untersuchungen wurden von uns nicht durchgeführt und sind auch in der Literatur nicht beschrieben.

Untersuchungen zur Atomemissionsspektrographie (AES) mit Gleichstrombogenanregung

Trotz der Tatsache, daß die Te I Resonanzlinie bei 214,3 nm die größte relative Lichtintensität besitzt, war das Linie–Untergrund-Verhältnis der Te I Linie

bei 238,5 nm für die analytische Anwendung günstiger. Dies hängt vor allem von der photographischen Registrierung und der Empfindlichkeit der verwendeten Photoplatten UV1 und WU 3 (ORWO, Wolfen, DDR) ab. Aus diesem Grund wurden die AES-Untersuchungen bei der Wellenlänge 238,5 nm durchgeführt.

Die verwendeten Elektrodenformen, die Stromstärke und die Belichtungszeit wurden sowohl für die Lösungs- als auch für die Feststoff-Analyse optimiert. Für die Lösungsspektralanalyse war eine schnelle Verdampfung (Stromstärke 15 A, Belichtungszeit 15 sec) günstiger, da bei langsamer Verdampfung die Reproduzierbarkeit infolge wegspritzender Matrixteilchen sank. Im Falle der Feststoffanalyse war die langsame Verdampfung günstiger. Bei einer Stromstärke von 6 A wurde eine Verdampfungszeit von 90 sec benötigt. Die analytischen Ergebnisse der Untersuchungen sind in der Tabelle 1 (Zeilen 12–14) enthalten.

Ein Vergleich von Zeile 12 und 13 zeigt, daß die UV-empfindliche Photoplatte ORWO UV 1 für die Bestimmungen am besten geeignet ist. Vergleicht man mit den analytischen Ergebnissen der AFS und AAS, so stellt man fest, daß die mit der AES erzielbaren absoluten Nachweisgrenzen um 2–3 Größenordnungen schlechter sind. Da die von uns eingesetzten Probemengen etwa 2 Größenordnungen über denen der AAS und AFS liegen, ergeben sich relative Nachweisgrenzen, die bis zu einer Größenordnung schlechter sind.

Durch Einsatz größerer Becherelektroden läßt sich die relative Nachweisgrenze für die direkte Feststoffanalyse noch verbessern. Bei Einsatz der Lösungsspektralanalyse ist die verwendete Matrixmenge von 5 mg ein Maximum. Größere Matrixmengen spritzen beim Zünden des Bogens von der Elekrodenoberfläche weg.

Ausführliche Untersuchungen matrixfreier Lösungen des Tellurs durch die Lösungsspektralanalyse wurden nicht durchgeführt, da bereits orientierende Versuche gezeigt hatten, daß die Abwesenheit des leicht ionisierenden Galliums im Plasma zu einer starken Depression der Emission der Te I Linien führt.

Allgemeine Schlußfolgerungen

Der Vergleich der Resultate der drei eingesetzten atomspektroskopischen Analysenmethoden zeigt, daß die Spurenbestimmung des Tellur in reinen Lösungen und auch in Gegenwart von $A^{III}B^{V}$-Halbleiter-Matrices bei Einsatz der AAS mit elektrothermischer Verdampfung der Probe in einer Graphitrohrküvette die besten absoluten und relativen Nachweisgrenzen lieferte.

Der Vorteil der AFS und der AES ist im größeren bestimmbaren Konzentrationsbereich zu sehen. Darüberhinaus besitzt die AES den Vorteil, daß Feststoffe direkt eingesetzt werden können und somit Kontaminationen, die vor allem durch Verunreinigungen beim Lösungsprozeß auftreten könnten, vollständig vermieden werden. Orientierende Versuche zum Einsatz von Festproben in der Graphitrohrküvette der AAS zeigten, daß keine Verbesserungen gegenüber der Lösungsanalyse erzielt werden konnten.

Auf der Basis der erhaltenen Resultate der AAS wurden analytische Bestimmungen an Te-dotiertem GaAs und GaP durchgeführt. Die Ergebnisse stimmten mit den Vorgaben überein. Sie wurden durch innere und äußere Dotierung auf ihre Richtigkeit überprüft.

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Summary—Methods are described for the determination of trace tellurium in acid solution in the absence and presence of the inorganic matrices As, P, Ga, GaP and GaAs and for the direct determination in solid GaP and GAs. The following methods were used: AAS with electrothermal atomization, AFS with electrothermal atomization, and AES with d.c. arc excitation. The conditions for each of the methods were optimized and the analytical results were compared. It is shown that AAS with electrothermal atomization gives the best absolute and also relative limit of detection for trace tellurium (90 pg Te, or 4 ppm Te in GaAs or GaP). Therefore this method is recommended for the determination of trace tellurium in very small samples of $A^{III}B^{V}$-semiconductors.

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PROTON-ACTIVATION TECHNIQUE FOR THE DETERMINATION OF ANTIMONY

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Summary—Proton-activation analysis has been applied to the determination of antimony. Thick-target yields and analytical sensitivities are given for the indicator-radionuclides ^{119m}Te, ^{119g}Te, ^{121m}Te, ^{121g}Te, ^{123m}Te, ^{120m}Sb and ^{122g}Sb for proton energies between 9 and 25 MeV. In irradiations with a 5-μA beam for 5 hr, followed by a specific separation of the indicator-radionuclides, limits of detection at the ppM level can be achieved. Data are given for the most significant interfering reactions. Antimony was determined instrumentally in bismuth of "very pure" grade and the results are compared with those obtained from two independent techniques.

In trace characterization of solid materials, activation techniques offer a number of advantages, of which freedom from reagent blanks and the possibility of removing surface contamination seem to be the most significant.

Antimony can be determined with high sensitivity by the thermal neutron reactions ^{121}Sb(n, γ) ^{122g}Sb and ^{123}Sb(n, γ) ^{124g}Sb. Use has been made of these reactions, in determinations of antimony in a variety of matrices, including metals,[1,2] diamond[3] and semiconductors.[4] However, in several instances, this technique has the disadvantage that lengthy separations are necessary and that difficulties can occur with the very high matrix activity. In view of these problems it would be convenient to have an additional powerful activation technique available. Our previous investigations[5] indicated that proton-activation analysis could be an interesting technique for the determination of antimony. In this paper, the thick-target yields and analytical sensitivities for proton-activation have been measured in the energy interval between 9 and 25 MeV for all reactions which might be of interest for activation analysis. In addition, the proton-activation technique has been applied to the instrumental determination of antimony in bismuth. The results have been compared with those obtained by neutron-activation analysis and atomic-absorption spectrometry.

EXPERIMENTAL

Charged particle activation

Thick targets of antimony of a purity grade better than 99.99% were irradiated for the determination of thick-target yields and for standardization. Analyses were performed on VP-grade samples of bismuth supplied by Material Research GmbH, Eching bei München, FRG. A pre-irradiation chemical etch was done with dilute nitric acid.

Irradiations were performed with 9–25-MeV protons at the Karlsruhe isochronous cyclotron. In the irradiation of antimony, the average beam currents were 100–300 nA for 60 sec. Beam-current measurements were made by integrating the charge collected in a Faraday cup. Bismuth samples for analysis were irradiated with 15-MeV protons in a water-cooled target-holder with a beam intensity of 2 μA, for 2 hr. In this case, a thin copper foil was used for monitoring the beam.

Gamma-rays were counted with a 75-cm^3 Ge(Li)-detector having an energy resolution of 1.9 keV FWHM at 1.332 MeV and a peak-to-compton ratio of 40:1. The low-energy γ-rays and X-rays were observed with a pure-germanium low-energy detector, 200 mm^2 in area and 7 mm in depth, and a total system resolution of 227 eV at 6.4 keV and 495 eV at 122 keV. The detectors were coupled with a 4000-channel pulse-height analyser.

Determination of antimony in bismuth by INAA

Bismuth samples of 100–150 mg and antimony standards were irradiated for 1 hr at a neutron flux of 8×10^{13} n.cm^{-2}.sec^{-1} in the FR-2 reactor of the Kernforschungszentrum Karlsruhe. After a cooling time of about 1 day and a post-irradiation etch with nitric acid, the samples were counted with the gamma-ray spectrometer described above. Both the ^{122g}Sb (564-keV γ-ray) and ^{124g}Sb (603-keV and 1691-keV γ-rays) were used as indicator radionuclides.

Determination of antimony in bismuth by AAS

The water and acids used were purified by sub-boiling distillation. About 0.5 g of bismuth was weighed and dissolved in nitric acid, which was then removed by adding hydrochloric acid and heating the solution in a water-bath. The sample solution was made 10*M* in hydrochloric acid and the antimony was separated from this solution with a 75% solution of tributyl phosphate in toluene. By using ^{124g}Sb as a radioactive tracer it was found that no detectable losses of antimony occurred during the whole procedure. The atomic-absorption measurements were made at 217.59 nm, by using a Perkin-Elmer Model 420 atomic-absorption spectrometer equipped with an HGA-76 graphite furnace, a deuterium background-corrector, an antimony hollow-cathode lamp and an AS-1 autosampler. The method of standard additions was used for standardization.

RESULTS AND DISCUSSION

Activation of antimony with protons

As can be seen from Table 1, in which the basic nuclear data are summarized, several analytically in-

Table 1. Nuclear data on production and properties of the indicator radionuclides in activation of antimony with protons

Reaction	Q-value, *MeV*	Half-life	Major X- and γ-rays, *keV*	Absolute intensity, %
^{121}Sb(p, n)^{121m}Te	−2.1	154.0 d	23.6 X	12.7
^{123}Sb(p, 3n)^{121m}Te	−17.8		27.4 X	27.5
			212.2 γ	81.0
^{121}Sb(p, n)^{121g}Te	−2.1	16.8 d	26.3 X	64.0
			29.8 X	13.0
^{123}Sb(p, 3n)^{121g}Te	−17.8		507.5 γ	19.4
			573.1 γ	79.1
^{123}Sb(p, n)^{123m}Te	−0.8	119.7 d	27.2 X	13.7
			27.5 X	26.8
			159.0 γ	83.5
^{121}Sb(p, pn)^{120m}Sb	−9.2	5.76 d	25.2 X	62.0
			28.6 X	13.0
			89.9 γ	77.0
			197.2 γ	89.0
			1023.1 γ	99.0
			1171.3 γ	100.0
^{123}Sb(p, pn)^{122g}Sb	−9.0	2.70 d	564.1 γ	63.0
^{121}Sb(p, 3n)^{119m}Te	−19.3	4.7 d	26.1 X	23.5
			26.3 X	46.0
			29.7 X	12.0
			153.0 γ	62.0
			270.6 γ	25.0
			1212.6 γ	67.0
^{121}Sb(p, 3n)^{119g}Te	−19.3	16.0 hr	644.1 γ	88.0
			699.6 γ	10.6

teresting reactions can be induced by protons in the energy interval considered. They are of the (p, n), (p, pn) and (p, 3n) type and can be induced for both stable nuclides of natural antimony, ^{121}Sb (57.3%) and ^{123}Sb (42.7%).

The thick-target yields measured for proton energies between 9 and 25 MeV are given in Table 2. They are expressed as the radioactivity in μCi produced at the end of irradiation for 1 hr with a proton-beam current of 1 μA. Figure 1 shows the dependence of the analytical sensitivities on the proton energy. The sensitivities are based on a 5-hr irradiation with a beam current of 5 μA and are expressed as the number of disintegrations per min at the end of the irradiation, per 1 ppm of antimony content. The values given in Table 2 and Fig. 1 are averages of two runs. The deviation from the mean value was in all cases less than 9%. However, the results presented can be used directly only for materials with an atomic number (or effective atomic number in the case of a complex target) close to that of antimony. Otherwise, corrections for the matrix effect must be made, by using factors obtained from the ranges[6] of the protons in pure antimony and in the given material.

From the results shown in Fig. 1, it can be seen that the ^{121}Sb(p, n)^{121g}Te reaction gives the best sensitivity up to a proton energy of about 19 MeV, the ^{123}Sb(p, pn)^{122g}Sb reaction between 19 and 23.5 MeV, and the ^{121}Sb(p, 3n)^{119g}Te reaction above 23.5 MeV. The indicator-radionuclides ^{121m}Te and ^{121g}Te are produced, up to a proton energy of about 18 MeV, exclusively by the ^{121}Sb(p, n) reaction. Above this proton energy the ^{123}Sb(p, 3n) reaction also contrib-

Table 2. Thick-target yields for proton-induced reactions of antimony

Reaction	Thick target yield, $\mu Ci.\mu A^{-1}.hr^{-1}$ Proton energy, *MeV* 9	12	15	18	21	25
^{121}Sb(p, n)^{121m}Te						
^{123}Sb(p, 3n)^{121m}Te	1.2	4.1	5.9	6.6	8.0	14.4
^{121}Sb(p, n)^{121g}Te						
^{123}Sb(p, 3n)^{121g}Te	15.0	50.3	64.4	71.5	79.0	108
^{123}Sb(p, n)^{123m}Te	1.3	3.4	4.4	5.0	5.2	5.4
^{121}Sb(p, pn)^{120m}Sb			0.2	2.5	10.3	29.8
^{123}Sb(p, pn)^{122g}Sb			6.9	44.9	129	286
^{121}Sb(p, 3n)^{119m}Te					1.9	179
^{121}Sb(p, 3n)^{119g}Te					14.5	1085

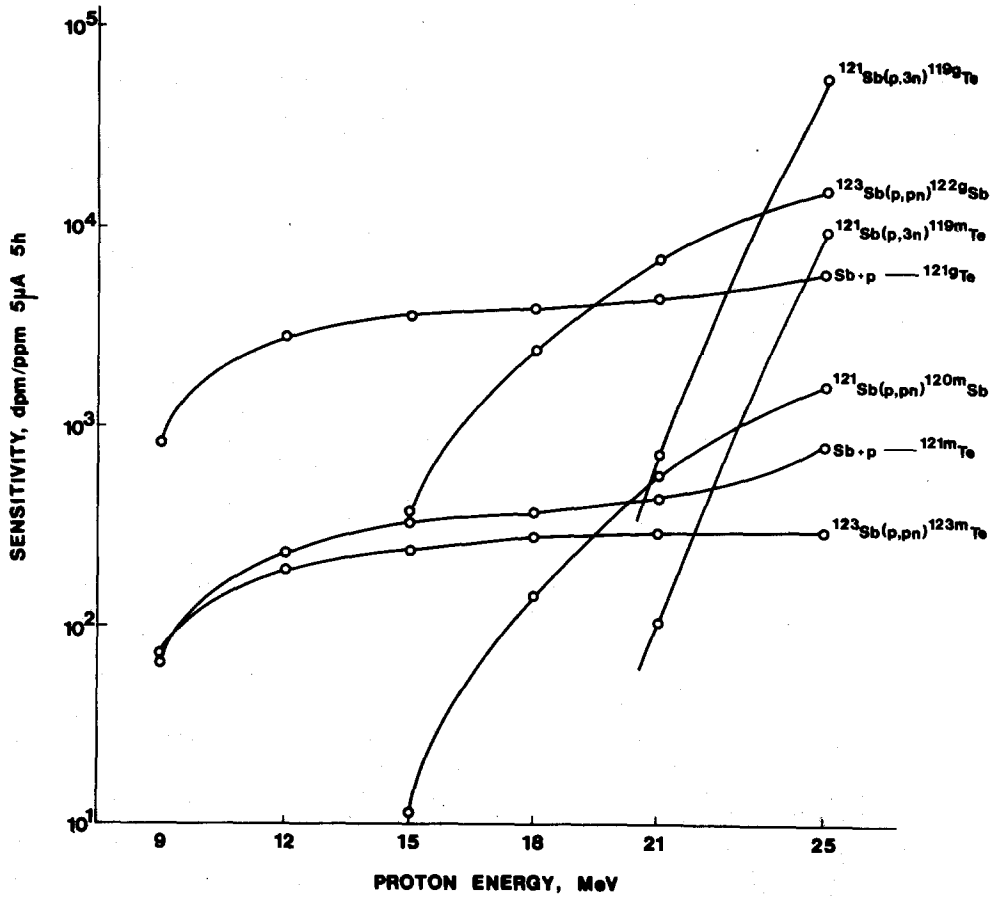

Fig. 1. Dependence of sensitivity on proton energy for different principal reactions.

utes to the production of these two nuclides. This explains the increase of the thick-target yields and sensitivities in the energy interval between 19 and 25 MeV.

There are several detection techniques of potential use for counting the indicator-radionuclides. Most of these radionuclides emit γ-rays which can be conveniently counted by conventional γ-ray spectrometry with a Ge(Li) detector. The 573.1-keV γ-ray is, in general, best suited for this purpose.

From Table 1, it can be seen that the decay of all product nuclides, excluding ^{122g}Sb and ^{119g}Te, is accompanied by the emission of X-rays of high intensity. For this reason, X-ray spectrometry with a low-energy-photon detector can also be a useful counting technique in the antimony determination. Several X-rays of different indicator-radionuclides, having the same or very similar X-ray energies, contribute to the formation of a peak. Figure 2 shows as an example an X-ray spectrum of pure antimony (irradiated with 12-MeV protons), measured with the low-energy-photon detector described before. At the same time, the 159.0-keV γ-ray of ^{123m}Sb and the 212.2-keV γ-ray of ^{121m}Te can be counted with this detector. After an irradiation with protons of higher energy (*e.g.*, 25 MeV), the 89.9-keV γ-ray of ^{120m}Sb and the 153.0-keV γ-ray of ^{119m}Te can also be counted simultaneously.

If intense activation of the matrix can be avoided, *e.g.*, by the choice of proton energy, detection limits significantly below 1 ppm can be achieved by using both γ-ray and low-energy-photon spectrometry. Which of these two counting techniques is better suited in a particular case, depends on the composition of the sample. However, the limit of detection can be considerably improved if the indicator-radionuclides of tellurium and/or antimony are specifically separated and counted with a non-energy-specific detector having high counting efficiency. Table 3 shows estimated limits of detection for different proton energies which could be obtained if the tellurium fraction containing all the tellurium indicator-radionuclides produced by the (p, xn) reactions, the antimony fraction containing the ^{120g}Sb and ^{122g}Sb produced by the (p, pn) reactions; and both the tellurium and antimony fractions were counted with an NaI(Tl) detector 5 hr after the end of the irradiation. By use of a well-type NaI(Tl) detector with 11-cm shielding of low-activity lead, in the counting of the tellurium indicator-radionuclides produced in an irradiation with 15-MeV protons, a limit of detection of 7 ppM (parts per milliard) was obtained.

In Table 4, the primary interference reactions which are energetically possible with a proton energy up

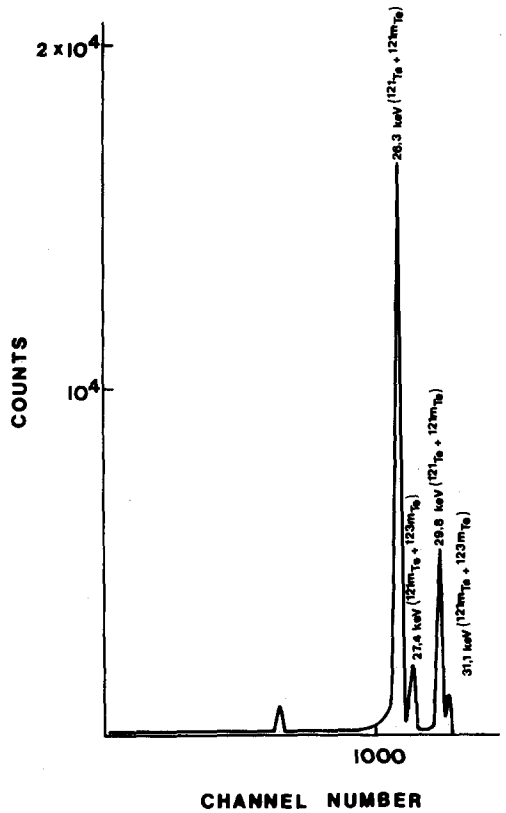

Fig. 2. X-Ray spectrum of proton-irradiated antimony observed with a low-energy photon detector. Irradiation time 1 min, proton energy 12 MeV, beam current 0.2 μA.

to 25 MeV are listed. Also given in the Table are the contributions of the most significant interfering reactions in the production of the indicator-radionuclides for 15-MeV and 25-MeV proton energies. These data are based on the assumption that the content

Table 3. Limits of detection achievable by radiochemical separations of the indicator radionuclides and counting with an NaI(Tl) well detector

Indicator radionuclides counted	Limit of detection*, *ppM* Proton energy, *MeV* 12	15	25
^{119m}Te, ^{119g}Te, ^{121m}Te, ^{121g}Te, ^{123m}Te	23	18	2
^{120m}Sb, ^{122g}Sb	—	530	9
^{119m}Te, ^{119g}Te, ^{121m}Te, ^{121g}Te ^{123m}Te, ^{120m}Sb, ^{122g}Sb	23	17	1.5

* Experimental conditions assumed: beam current 5 μA, irradiation time 5 hr, time between the end of the irradiation and the beginning of the counting 5 hr, chemical yield of the tellurium and antimony separation approx. 100%. Counting with a well-type 3 × 3 in. NaI(Tl) detector with good shielding. The limit of detection (ppM = parts per milliard) is the content of antimony which gives 100 counts per min.

of antimony and of the interfering tellurium is the same and they were estimated by using the systematics of thick-target yields.[7] When tellurium isotopes are used as indicator-radionuclides, primary interfering reactions can, arise only from tellurium and iodine. As can be seen from Table 4, the interference of tellurium can be neglected up to a proton energy of 15 MeV if the contents of antimony and tellurium are at about the same level. The low extents of interference are mainly due to the low abundances of the relevant target nuclides in natural tellurium. The same is true if a proton energy of 25 MeV is used, as in this case ^{119m}Te and ^{119g}Te are the dominant indicator-radionuclides. Even if all tellurium radionuclides are counted together (with an NaI(Tl) detector), after an irradiation with 25-MeV protons the interference of tellurium is below 1%, since the contribution of ^{121m}Te, ^{121g}Te and ^{123m}Te to the total

Table 4. Possible primary interference reactions in activation of antimony with protons

Analytical reaction	Interfering reaction	Q-value *MeV*	Isotopic abundance, %	Contribution to the production of the indicator-radionuclide, % Proton energy, *MeV* 15	25
^{121}Sb(p, n)^{121m}Te ^{123}Sb(p, 3n)^{121m}Te	^{122}Te(p, pn) ^{121m}Te	−10.1	2.4	<0.15	<4
^{121}Sb(p, n)^{121g}Te ^{123}Sb(p, 3n)^{121g}Te	^{122}Te(p, pn)^{121g}Te	−10.1	2.4	<0.15	<4
^{123}Sb(p, n)^{123m}Te	^{124}Te(p, pn)^{123m}Te	−9.4	4.6	<0.4	<22
	^{127}J(p, αn)^{123m}Te	−11.2	100.0		
^{121}Sb(p, 3n)^{119m}Te	^{120}Te(p, pn)^{119m}Te	−10.3	0.09		<0.5
^{121}Sb(p, 3n)^{119g}Te	^{120}Te(p, pn)^{119g}Te	−10.3	0.09		<0.5
^{121}Sb(p, pn)^{120m}Sb	^{120}Sn(p, n)^{120m}Sb	−3.5	32.8		
	^{122}Sn(p, 3n)^{120m}Sb	−18.5	4.7		
	^{123}Te(p, α)^{120m}Sb	+4.1	5.8		
	^{124}Te(p, αn)^{120m}Sb	−5.3			
	^{125}Te(p, α2n)^{120m}Sb	−11.9	7.0		
	^{126}Te(p, α3n)^{120m}Sb	−21.0	18.7		
^{123}Sb(p, n)^{122g}Sb	^{122}Sn(p, n)^{122g}Sb	−2.4	4.7		
	^{124}Sn(p, 3n)^{122g}Sb	−16.8	5.8		
	^{125}Te(p, α)^{122g}Sb	+4.2	7.0		
	^{126}Te(p, αn)^{122g}Sb	−4.9	18.7		
	^{128}Te(p, α3n)^{122g}Sb	−20.0	31.8		

indicator-radionuclide activity is relatively low (~9%). At a proton energy of 12 MeV a 100-fold ratio of tellurium to antimony is tolerable, and at a proton energy of 9.5 MeV no interference from tellurium can occur. The extent of the interference of iodine can be expected to be even lower than that of tellurium. In any case, this element is seldom present as an impurity in metals or other materials.

With respect to primary interferences, the utilization of the indicator-radionuclides ^{120m}Sb and ^{122g}Sb produced from antimony by (p, pn) reactions is very disadvantageous, as extremely strong interference arises from tin by the ^{120}Sn(p, n)^{120m}Sb and the ^{122}Sn(p, n)^{122g}Sb reactions and tin occurs frequently as an impurity together with antimony. In addition, tellurium interferes to a larger extent as a result of (p, αxn) reactions than it does by (p, pn) reactions using tellurium indicator-radionuclides. Therefore, this modification of proton-activation analysis for antimony has little practical significance. Of much less significance in this particular case are interference reactions induced by secondary neutrons.

Determination of antimony in bismuth

The applicability of the proton-activation technique is exemplified by the determination of antimony in bismuth of VP grade. In the irradiation of bismuth with 15-MeV protons, because of the low saturation factors, high coulomb-barrier and low irradiation emission in the decay, no dominant radioactivity is produced from the matrix and the analysis is easily done by an instrumental procedure. Owing to the lack of bismuth reference standards, the accuracy of the proton-activation technique was checked by comparing the results with those obtained from two independent analytical methods. The following results have been obtained for the determination of antimony, by using all three analytical reactions at proton energy of 15 MeV:

2.5 ± 0.25 ppm by instrumental proton-activation analysis (IPAA)

2.6 ± 0.3 ppm by instrumental neutron-activation analysis (INAA)

3.4 ± 0.3 ppm by atomic-absorption spectrometry (AAS).

For each technique, the results represent averages of three determinations on separate samples, for which the average deviations are also given.

There is good agreement between the results obtained from IPAA and INAA. However, the result of IPAA is 26% lower than that obtained from AAS. Taking into consideration the deviations obtained with both techniques, the upper limit of the IPAA-value differs from the lower limit of the AAS-value by 10%. Of course, this degree of error also includes uncertainties due to inhomogeneities in the distribution of antimony in the bismuth sample. In the determination of antimony in bismuth, of the three techniques applied, proton activation has the best limit of detection, 0.05 ppm, for counting of the 573.1-keV γ-rays, after a delay time of about 5 days. The limit of detection by INAA under the optimum experimental conditions was found to be 0.1 ppm and that of the atomic-absorption analysis about the same.

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UNTERSUCHUNGEN ZUR ATOMSPEKTROSKOPISCHEN SPURENANALYSE IN $A^{III}B^{V}$-HALBLEITER-MIKROPROBEN—V

BESTIMMUNG VON SELEN- UND TELLURSPUREN IN ANORGANISCHEN MATRICES DURCH AAS MIT DIREKTER ELEKTROTHERMISCHER VERDAMPFUNG IN EINER GRAPHITROHRKÜVETTE UND DURCH AAS IM QUARZROHRATOMISATOR NACH HYDRIDERZEUGUNG—UNTERSUCHUNG DER MATRIXEFFEKTE UND METHODENVERGLEICH

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Zusammenfassung—Es wird die Bestimmung von Se- und Te-Spuren durch AAS mit Erzeugung flüchtiger Hydride und deren Atomisierung in einem beheizten Quarzrohr und durch AAS mit direkter elektrothermischer Atomisierung in einer Graphitrohrküvette beschrieben. Die apparativen Parameter und die Bedingungen wurden optimiert. Für reine saure Lösungen ergaben sich für die Se-AA bei Anwendung der Hydridtechnik und für die Te-AA bei Anwendung der Graphitrohrküvette Vorteile. Der Einfluß der $A^{III}B^{V}$-Matrices und anderer Substanzen, die ebenfalls flüchtige Hydride bilden, auf die Bestimmung des Selen und Tellur wird untersucht. Bei Verwendung der Hydridtechnik fanden wir, daß die Hauptursachen für die Depression der AA-Signale in der Bildung unlöslicher Verbindungen zwischen der Matrix und dem H_2Se bzw. H_2Te und dem Verlust an $NaBH_4$ durch reduzierbare Verbindungen bestehen. Im Fall der Graphitküvette sind die Hauptgründe für die Depression die Bildung stabiler Moleküle im Plasma und die Zunahme des Streulichtes. Die analytischen Möglichkeiten der Methoden werden verglichen. Die Vorteile und Nachteile werden beschrieben.

Sowohl Selen als auch Tellur werden zur Erzielung bestimmter elektrischer und optoelektronischer Eigenschaften bei $A^{III}B^{V}$-Halbleitern als Zusätze eingesetzt. Zur Kontrolle der gewonnenen Stoffe ist die analytische Bestimmung von Spuren dieser Elemente in anorganischen Mikroproben erforderlich (vergleich auch Mitteilung IV[1]). Zur Lösung dieser analytischen Problematik erschien die AAS am geeignetsten, obwohl infolge der angeführten Probleme die AAS für die Se- und Te-Spurenbestimmung keine Idealmethode ist:

1. Die Resonanzlinien dieser Elemente liegen im fernen UV. Dies führt zu einem starken Untergrund infolge der in diesem Spektralgebiet in Gegenwart beliebiger anorganischer Matrices stark zunehmenden Lichtstreuung und Molekülabsorption.

2. Beide Elemente bilden thermisch relativ stabile zweiatomige Moleküle und sind gleichzeitig leicht verdampfbar. Dies führt zu Problemen bei der Optimierung der thermischen Bedingungen und gegebenenfalls zu einer relativ niedrigen Atomkonzentration im Plasma.

3. Die Hohlkathodenlampen dieser Elemente sind wegen der leichten Verdampfbarkeit und schweren Anregbarkeit relativ lichtschwach. Elektrodenlose Entladungslampen besitzen Vorteile.

Unter Berücksichtigung dieser Probleme und den für Tellur bereits erzielten Ergebnissen[1] sollte getestet werden, ob die bei der Anwendung der Hydridmethode zum Teil erzielbaren chemischen Spur–Matrix-Trennungen gegenüber der direkten elektrothermischen Verdampfung in einer Graphitrohrküvette bessere relative Nachweisgrenzen ergeben.

Sowohl für die Anwendung der direkten elektrothermischen Atomisierung als auch der Hydridmethode auf die Bestimmung von Selen- und Tellurspuren sind eine Reihe von Veröffentlichungen erschienen, die hier nur zum Teil erwähnt werden können.

Bei der direkten elektrothermischen Atomisierung in einer Graphitrohrküvette führte die Stabilisierung des leicht verdampfbaren Selens durch Nickelsalze[2–4] und auch die chemische Spur–Matrix-Trennung durch Extraktion[5] zur Verbesserung der analytischen Ergebnisse. Die erzielten absoluten Nachweisgrenzen liegen bei 10^{-10} g. Hinsichtlich des Tellurs verweisen wir auf die Mitteilung IV.[1] Auch über die genannte Problematik der Dissoziation zweiatomiger Spezies wird berichtet.[6]

Seit mehreren Jahren findet man in der Literatur Mitteilungen über die Anwendung der Hydridtechnik.

Mitteilung IV: *Talanta*, 1979, **26**, 737.

Für die nachfolgende Atomisierung wurden anfangs vor allem untergrundarme H_2–Ar–Luft-Flammen eingesetzt.[7,8] Die Anwendung auf reale analytische Probleme[9–12] zeigte, daß die Methode praktizierbar ist. Die absoluten Nachweisgrenzen lagen im Nanogrammbereich. Gegenüber der einfachen Flammenatomisierung konnten somit Verbesserungen erzielt werden.

Neben der Atomisierung der Hydride in Flammen wurden für diesen Zweck auch beheizte Quarzrohre unterschiedlicher Dimension eingesetzt.[13–15] Auch diese Variante der Methode wurde in einigen Fällen für die analytische Untersuchung realer Proben eingesetzt.[16–18] Die erzielten absoluten Nachweisgrenzen liegen zwischen 10^{-9} und 10^{-10} g.

Obwohl über den Einsatz der Hydridtechnik auf reale analytische Probleme berichtet wurde, gibt es nur sehr wenig Untersuchungen über den Einfluß von Matrices auf die Bestimmungsmethode. Aus den Arbeiten von Smith,[19] Robert[20] und Pierce und Brown,[21] die jeweils die Flamme zur Atomisierung der Hydride verwendeten, geht hervor, daß eine Vielzahl von Matrixeffekten vorhanden sind, die nur zum Teil erklärt wurden.

Da bisher mit den beheizten Quarzrohrküvetten bessere absolute Nachweisgrenzen erzielt wurden, wurde diese Technik zum Vergleich mit der direkten elektrothermischen Atomisierung für die Selen- und Tellurspurenanalyse in Mikroproben ausgewählt. Systematische Untersuchungen sollten vor allem zur Klärung des Einflusses unterschiedlicher, auch hydridbildender anorganischer Matrices durchgeführt werden.

EXPERIMENTELLER TEIL

Apparatives

1. Hydridtechnik mit Atomisierung im Quarzrohr.

Spektrometer: Einstrahl-Einkanal-AA-Spektrometer, AAS 1, VEB Carl Zeiss, Jena, DDR.

Atomisator: Quarzrohrküvette, Eigenbau.[22] Länge: 145 mm, inn. ϕ: 6 mm, Wandstärke: 1 mm. Heizung: Kanthaldrahtwicklung, ϕ 0,4 mm. Temperaturen: max. 1000°.

Hydriderzeugung: Halbmikroapparatur, Eigenbau, vgl. Abb. 1.

Lichtquelle: Se-EDL, Pye-Unicam, England. Leistung: 7 W, spektrale Bandbreite: 0,1 nm, Wellenlänge: 196,0 nm. Anregungsgerät für EDL, Pye-Unicam, England. Adapter, Eigenbau. Te-HKL, Jarrell-Ash, USA. 5 mA, Spektrale Bandbreite: 0,2 nm, Wellenlänge: 214,3 nm.

Bemerkung: Es wurde keine Untergrundkompensation durchgeführt.

2. Elektrothermische Atomisierung in der Graphitrohrküvette.

Spektrometer: Zweikanal-Zweistrahl-AA-Spektrometer, Typ 811, Jarrell-Ash, USA.

Atomisator: Graphitrohrküvette 1268, Beckman, USA.

Lichtquelle: Te-HKL, vgl. Mitt. IV. Se-EDL, Pye-Unicam, England. Leistung: 9 W, spektrale Bandbreite: 0,1 nm, Wellenlänge: 196 nm. Die Untergrundkompensation erfolgte nach der Zweilinienmethode mit der Se-EDL: Wellenlänge: 199,3 nm, spektrale Bandbreite: 1 nm. Adapter für Anregung der EDL, Eigenbau.

Elementkonstanten

Tellur: vgl. Mitteilung IV.[1]

Selen: Ionisierungspotential: 9,75 eV; Siedepunkt: 685°C.

Grundzustand: $4p^4\ ^3P_2$.

Übergang bei 196 nm: $4p^4\ 3P_2 \rightarrow 5s\ ^3S_1$ (E_a = 6,32 eV).

Lösungen

Durch oxydatives Lösen von reinem Selen oder Tellur in konzentrierten Säuren, durch nachfolgendes Eindampfen und Aufnehmen in 1*M* Salzsäure wurden die Stammlösungen gewonnen, die 1 mg Se bzw. Te pro ml 1*M* Salzsäure enthielten. Durch entsprechendes Verdünnen wurden die Untersuchungslösungen erhalten. Zur Herstellung der erforderlichen Matrixlösungen vgl. Mitteilungen II[22] und IV.[1] In ähnlicher Weise wurden für die Untersuchung des Matrixeinflusses von Wismut, Indium, Germanium, Antimon, Zinn und Tellur bzw. Selen Lösungen bestimmter Konzentration in 1*M* Salzsäure hergestellt.

Durch Auflösen von $NaBH_4$ (Ferak, Westberlin) in 1%iger Natronlauge wurde die 1 bzw. 2%ige Reduktionslösung gewonnen. Diese Lösung war mehrere Tage stabil.

Allgemeine Arbeitsweise

Hydridtechnik. Die von uns speziell für kleine Probevolumina hergestellte Hydriderzeugungsapparatur ist in der Abbildung 1 dargestellt. In das Probegefäß (A) wird die saure Probelösung und in das Vorratsgefäß (D) die $NaBH_4$-Lösung gegeben. Danach wird die Apparatur über den Einlaß (E) zur Entfernung der Luft mit Argon gespült. Durch Umschalten des Dreiwegehahns (B) wird der Argoneinlaß von (E) auf (D) verlegt. Dadurch wird die $NaBH_4$-Lösung in die Probelösung gedrückt und schnell mit ihr vermischt. Das entstehende Hydrid wird durch das Argon ausgetrieben und zum Quarzrohratomisator transportiert. Auf diese Weise wurde die von Pierce und Brown[21] vorgeschlagene Lösungsreihenfolge (Säurezugabe

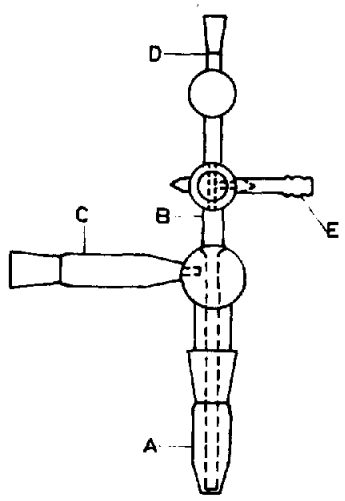

Abb. 1. Hydriderzeugungsapparatur für kleine Probemengen. A—Reaktionsgefäß (5–7 ml), D und E–Argoneinlaß, umschaltbar durch Dreiwegehahn B, D—Eingabe der $NaBH_4$-Lösung, C—Argon und Hydridaustritt zum Quarzrohratomisator.

vor $NaBH_4$-Zugabe) realisiert. Wichtig ist, daß das Probegefäß sofort nach der Analyse zuerst mit konzentrierter Salzsäure und danach mit destilliertem Wasser gespült wird. Andernfalls treten bei den folgenden Versuchen infolge vorhandener $NaBH_4$-Reste depressive Effekte bei der Selen- bzw. Tellurbestimmung auf.

Elektrothermische Atomisierung. Für diese Untersuchungen wurden Lösungsvolumina von 0,01 ml, die die Spuren- und Matrixelemente in den erforderlichen Konzentrationen enthielten, in die Graphitrohrküvette gegeben, getrocknet, verascht und atomisiert.

OPTIMIERUNG DER BEDINGUNGEN UND DER APPARATIVEN PARAMETER

Hydridtechnik

Folgende Bedingungen und Parameter mußten für die Bestimmungen optimiert werden:

Strömungsgeschwindigkeit des Transportgases Argon.

Volumen und Azidität der Probelösung, Volumen und Konzentration der $NaBH_4$-Lösung.

Strömungsgeschwindigkeit des Argons. Mit der Erhöhung der Strömungsgeschwindigkeit des Argons ergeben sich sowohl positive, d.h. das AA-Signal erhöhende Faktoren, z.B.,

1. schneller und vollständiger Transport der $NaBH_4$-Lösung in die Probe;
2. schnelle und innige Mischung der Lösungen ergibt eine schnelle Hydridbildung;
3. schnelles Austreiben des Hydrids;

als auch negative, d.h. das AA-Signal erniedrigende Faktoren, z.B.,

1. ein zu großes Argon–Hydrid-Volumenverhältnis führt zur Reduzierung der Atomkonzentration im Quarzrohratomisator;
2. eine geringe Aufenthaltsdauer der Gase im Quarzrohratomisator führt zur schlechten Erwärmung und damit schlechten Atomisierung und auch zur geringen Aufenthaltsdauer der Atome im Plasma.

Experimentell wurde diese Tendenz bestätigt. Die optimale Strömungsgeschwindigkeit lag für unsere Apparatur bei 30 l./hr.

Volumen und Azidität der Probelösung, Volumen und Konzentration der $NaBH_4$-Lösung. Auch in diesem Fall gibt es mit der Veränderung der Parameter positive und negative Effekte. Geringe Volumina lassen sich besser mischen und ergeben hohe Hydridkonzentrationen.

Begrenzend für diesen Faktor ist: 1. das mögliche Verhältnis der Volumina der Lösung und der Apparatur und 2. die überhaupt möglichen Konzentrationen. Weiterhin hängt die Schnelligkeit und Vollständigkeit der Hydridbildung direkt von der Säurekonzentration[7,23] und von der $NaBH_4$-Konzentration ab. Für die Erzeugung des Hydrids wird jedoch in jedem Fall nur ein sehr kleiner Teil des $NaBH_4$ (etwa 0,1% und weniger) verbraucht. Der übrige Teil wird in Wasserstoff überführt, welches sich mit dem Transportgas Argon vermischt. Das in die Gasphase überführt Hydrid wird durch eine zu große Menge Wasserstoff zu stark verdünnt. Wenn man ohne zusätzliches Ausfrieren des Hydrids arbeitet, letzteres führt im allgemeinen zu einer Erniedrigung der Analysenfrequenz, so führt dieser Effekt zu einer Verminderung der Atomkonzentration und der Aufenthaltsdauer der Atome im Quarzrohratomisator. Beide Einflüsse wurden durch das Experiment bestätigt. Die optimalen Bedingungen ergaben sich bei uns zu: 0,25 ml 1%ige $NaBH_4$-Lösung in 1%iger Natronlauge; 0,15–0,2 ml Probelösung (1*M* an HCl).

Elektrothermische Atomisierung

In diesem Fall müssen vor allem die thermischen Bedingungen optimiert werden. Die Abbildung 2 zeigt die Abhängigkeit des Selen- bzw. Tellur-AA-Signals von der Veraschungstemperatur (bei optimaler Atomisierungstemperatur) (Kurven 1) und von der Atomisierungstemperatur (bei beliebiger Veraschungstemperatur) (Kurven 2). Es ist zu sehen, daß die am Gerät einstellbare Veraschungstemperatur zu keinen Se- bzw. Te-Verlusten führten und daß die Atomisierungstemperaturen zum Zweck der möglichst vollständigen Dissoziation molekularer Spezies so hoch wie möglich sein sollten. Zu bemerken ist, daß die angegebenen Temperaturen von uns nicht pyrometrisch gemessen wurden, sondern nur einem Voltmeter des Gerätes, welches eine Temperaturskala hatte, entnommen wurden. Die wahren Temperaturen liegen offensichtlich etwas niedriger als die angegebenen Werte. Die Veraschungszeit lag jeweils bei 10 sec. Erhöht man diese Zeit, so treten Selen- und auch Tellur-Verluste auf. Daraus ist zu schlußfolgern, daß nach 10 sec Veraschungszeit noch nicht die maximale

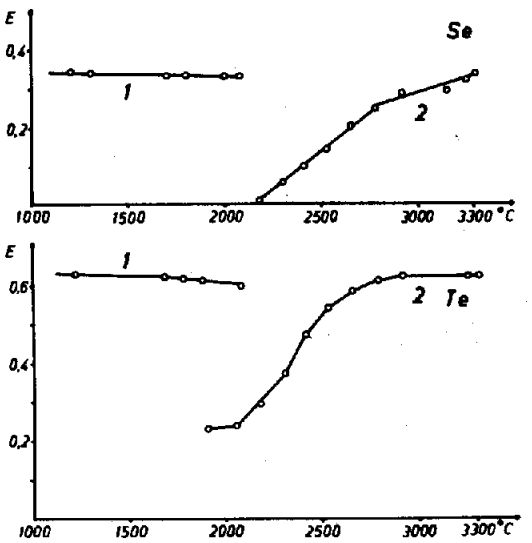

Abb. 2. Abhängigkeit des Se- bzw. Te-AA-Signals von den thermischen Bedingungen der Graphitrohrküvette. Kurven 1: variierte Veraschungstemperatur (10 sec), konstante Atomisierungstemperatur (3300°C, 10 sec). Kurven 2: konstante Veraschungstemperatur (1000°C, 10 sec), variierte Atomisierungstemperatur (10 sec). Se: 3,8 ng; Te: 10 ng.

Tabelle 1. Ergebnisse der Bestimmung von Selen und Tellur durch AAS bei Einsatz reiner 1*M* salzsaurer Lösungen

Methode	Element	Nachweisgrenze (3*s*) absolut, *pg*	relativ, *ng/g*
Hydridmethode	Se	90	0,6†
Graphitrohrküvette	Se	225	11§
Hydridmethode	Te	1000	7†
Graphitrohrküvette	Te	90	4§

* Vergleich auch Mitteilung IV.[1]
† Bezogen auf 0,15 ml 1*M* HCl.
§ Bezogen auf 0,02 ml 1*M* HCl.

Temperatur erreicht ist. Auch in Gegenwart anorganischer Matrices traten keine Se- bzw. Te-Verluste während der Veraschungsphase auf. Es wurde sogar festgestellt, daß einige Matrices, wie Bi, Sb, Ga u.a., zum Teil vor dem Selen bzw. Tellur verdampfen, wodurch die Matrixkonzentration in der Atomisierungsphase vermindert wird. Diese Effekte wurden nicht näher untersucht. Offensichtlich handelt es sich um eine thermische Stabilisierung der Spuren wie sie schon früher beschrieben wurde.[2,3,24,25]

Als optimale Bedingungen ergaben sich: Veraschungsphase 10 sec, 800–1400°; Atomisierungsphase 10 sec, 3300°.

ANALYTISCHE RESULTATE BEI EINSATZ REINER LÖSUNGEN

Zur Überprüfung der Leistungsfähigkeit der einzelnen Apparaturen und Methoden, wurden die Nachweisgrenzen in reinen, 1*M* salzsauren Lösungen für Selen- und Tellur-Spurenbestimmungen ermittelt (vgl. Tab. 1).

Vergleicht man die Resultate mit den Literaturwerten, so ergibt sich für Selen eine kleine Verbesserung. Für Tellur wurden die bischer erzielten Werte bestätigt (vergleich auch Mitteilung IV[1]). Im Falle des Selen liefert die Hydridmethode, im Falle des Tellur die direkte elektrothermische Atomisierung in der Graphitrohrküvette die bessere absolute Nachweisgrenze. Dieses Ergebnis ist einerseits mit der besseren und schnelleren Bildung des gegenüber dem Tellurwasserstoff stabileren Selenwasserstoff bei Anwendung der Hydridmethode und andererseits mit der stärkeren Dissoziation der gegenüber den molekularen Se-Spezies thermisch instabileren molekularen Te-Spezies in der Graphitrohrküvette zu erklären. Die erzielten Resultate erlauben es, beide Methoden für den Einsatz zur Spurenbestimmung in Mikroproben zu testen.

UNTERSUCHUNG DES EINFLUSSES ANORGANISCHER MATRICES

Hydridtechnik

In der Tabelle 2 wird eine Übersicht über die möglichen Matrixeffekte, die bei der Anwendung der Hydridmethode auftreten können, gegeben. Gleichzeitig wird für die von uns eingesetzten Matrices—es handelt sich um die Komponenten von $A^{III}B^{V}$-Halbleiterverbindungen und um andere hydridbildende Matrices—eine qualitative Bewertung der möglicherweise eintretenden Effekte gegeben.

In den Abbildungen 3 und 4 werden die experimentellen Ergebnisse für den Einfluß verschiedener Matrices dargestellt. Ein Vergleich der Abbildungen 3 und 4 zeigt, daß bis auf wenige Ausnahmen—z.B. die Einordnung des Selen bzw. des Tellur in die entsprechende Reihe—die Matrixeinflüsse auf die Se- und Te-AA-Signale identisch sind. Vergleicht man die

Tabelle 2. Übersicht über die möglichen Ursachen der depressiven Matrixeffekte bei der Hydridmethode

Art des Matrixeinflusses	Matrices GaP	In	Bi	Ge	As	Te	Se	Sb	Sn
A. Signaldepression									
1. Verbrauch des Reduktionsmittels durch die Matrix									
(*a*) Reduktion zu Verbindungen mit niederem Oxydationsgrad	−	+	−	+	+	+	+	+	+
(*b*) Reduktion zum Element	−	(+)	+	−	(+)	(+)	(+)	+	+
(*c*) Reduktion zum Hydrid	−	−	(+)	(+)	+	+	+	+	+
2. Reaktionen der Matrices mit Selen und Tellur									
(*a*) Matrix (M) + $H_2Se \rightarrow MSe$	−	+	+	−	+	−	−	+	+
(*b*) Reduzierte Matrix (M^z) + $H_2Se \rightarrow M^zSe$	−	(+)	−	+	+	−	−	+	+
B. Vergrößerung der Intensität des Untergrundes									
1. Bildung leichtflüchtiger Matrix hydride	−	−	(+)	(+)	+	+	+	+	(+)
2. Molekülbildung und Kondensation der Matrices im Plasma	−	−	(+)	(+)	(+)	(+)	(+)	(+)	(+)

\+ Einfluß vorhanden, (+) Einfluß möglicherweise vorhanden, − kein Einfluß.

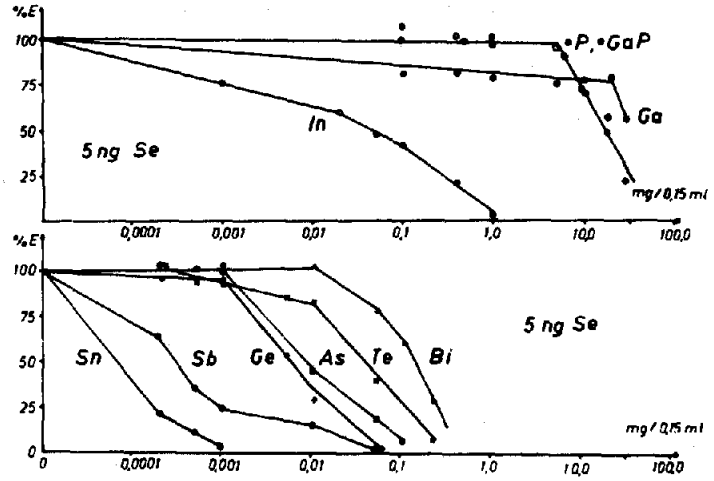

Abb. 3. Abhängigkeit der Se-AA von der Gegenwart anorganischer Matrices bei Einsatz der Hydridmethode und Atomisierung im Quarzrohratomisator.

Bewertung der Tabelle 2 mit den Ergebnissen der Abbildungen 3 und 4, so ergibt sich ebenfalls eine Übereinstimmung, denn die Anzahl der mit + versehenen, möglichen Matrixeffekte korreliert mit dem experimentellen Ergebnis.

Die Matrices Ga^{3+}, P (als PO_4^{3-}) und GaP (als Ga^{3+}/PO_4^{3-}) bewirken praktisch erst bei sehr hohen Konzentrationen eine Depression des AA-Signals. Die Ursachen dieser Depressionen sind vor allem auf die veränderten Eigenschaften der Lösung und eventuell auch auf Spurenverunreinigungen der Matrices zurückzuführen.

In Gegenwart von In^{3+} tritt bereits bei niedrigeren Konzentrationen (gegenüber dem chemisch ähnlichen Ga^{3+}) eine depressive Wirkung auf das AA-Signal auf. Dies ist damit zu erklären, daß In^{3+} leichter zum In^{+} reduziert werden kann als das Ga^{3+} zum Ga^{+}. Obwohl auch das In^{+} in wäßrigen Lösungen nicht stabil ist, würde bei der Reduktion $NaBH_4$ verbraucht. Somit steht es nicht für die Reduktion der zu bestimmenden Spuren zur Verfügung. Wir sind allerdings der Auffassung, daß die Hauptursache der depressiven Wirkung des Indiums in der Bildung von schwerlöslichem In_2Se_3 bzw. In_2Te_3 zu suchen ist. Diese Verbindungen sind auch in verdünnten Säuren noch stabil. Die übrigen getesteten Matrices bilden jeweils selbst flüchtige Hydride. Da die Einflüsse sich jedoch über 3 Zehnerpotenzen der Konzentrationswerte bemerkbar machen, kann die Hydridbildung und der damit verbundene $NaBH_4$-Verlust nicht die einzige Ursache für die depressiven Erscheinungen sein.

Wismut bildet nur schwer das nicht sehr stabile Hydrid BiH_3. Es wird jedoch durch $NaBH_4$ zum Metall reduziert. Auch beim Wismut ist der Haupteinfluß die Bildung schwerlöslicher Telluride und

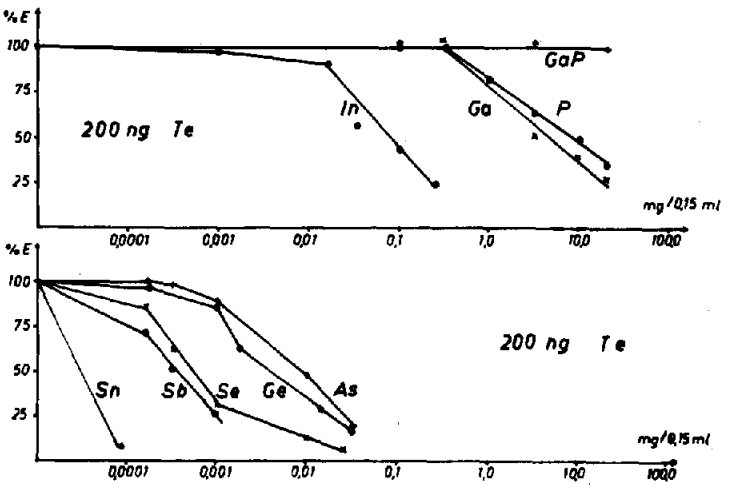

Abb. 4. Abhängigkeit der Te-AA von der Gegenwart anorganischer Matrices bei Einsatz der Hydridmethode und Atomisierung im Quarzrohratomisator.

Selenide. Besonders bei den Untersuchungen zur Te-AA wurde festgestellt, daß durch die Gegenwart von Bi^{3+} als Matrix die gesamte Hydriderzeugungsapparatur sehr schnell "vergiftet" wird, d.h. auch bei nachfolgenden Messungen ohne Bi^{3+}-Matrix werden nur stark reduzierte Te-AA-Signale erhalten. Dies läßt sich damit erklären, daß ein Teil des Bi^{3+} in BiH_3 verwandelt wurde, welches sich infolge seiner Instabilität leicht an den Glaswänden zersetzt und dort einen unsichtbaren, aktiven B-Film bildet. Dieses Wismut reagiert schnell mit den vorbeiströmenden Spuren des Tellur- bzw. auch des Selenwasserstoffs.

Arsen- und Germanium-Matrices haben auf Te- und Se-AA-Signale eine ähnliche depressive Wirkung. Da sich jedoch Arsenwasserstoff bedeutend leichter als Germaniumwasserstoff bildet, sollte hierin nicht die Hauptursache der depressiven Wirkung gesehen werden. Diese besteht u.E. wiederum in der Bildung unlöslicher Verbindungen. Für Germanium ist bekannt, daß ein stabiles, in 3*M* Salzsäure unlösliches Selenid des zweiwertigen Germaniums (GeSe) existiert. Die Selenide und Telluride des 3- und 5-wertigen Arsens sind ebenfalls unlöslich. Eine exakte Detailbewertung der vielen Möglichkeiten ist schwierig: z.B sind die Selenide und Telluride des Arsens stabiler als die des Germaniums und andererseits bildet sich AsH_3 schneller als GeH_4. Letzteres führt zu stärkeren Arsen-Verlusten in der Lösung und somit zu einer gegenüber Germanium geringeren Bildung unlöslicher Produkte. Die ähnliche Wirkung dieser beiden Matrices ist offensichtlich rein zufällig.

Die Tatsache, daß Zinn- und Antimon-Matrices sowohl auf die Se-AA als auch auf die Te-AA den stärksten Einfluß ausüben, unterstützt die gegebenen Erklärungen. Beide Elemente bilden gegenüber dem Arsen die entsprechenden Wasserstoffverbindungen SbH_3 und SnH_4 langsamer. Diese Verbindungen sind außerdem instabiler als das Arsin. Andererseits bilden sie ebenfalls schwerlösliche Selenide und Telluride. Auch die Bildung thermisch stabiler, molekularer Spezies im Quarzrohratomisator ist möglich (s.u.). In Gegenwart von Zinn tritt ein gleicher "Vergiftungs"-Effekt wie beim Wismut auf. Die Apparatur muß mit Königswasser ausgekocht werden, ehe sie wieder verwendet werden kann. Die Zersetzung des gebildeten Zinnhydrids erfolgt sowohl auf dem Wege zum als auch im Quarzrohratomisator.

Zusammenfassend ergibt sich aus den Ergebnissen, daß der wesentliche Einfluß anorganischer Matrices auf die Se-AA bzw. Te-AA in der Bildung schwerlöslicher Verbindungen mit den entstehenden Wasserstoffverbindungen und in der Hydridbildung der Matrices selbst zu sehen ist.

Zuletzt soll auf den unterschiedlichen Einfluß der Se-Matrix auf die Te-AA und der Te-Matrix auf die Se-AA eingegangen werden. Dieses Resultat ist vor allem mit der unterschiedlichen Bildungsgeschwindigkeit und Stabilität der zugehörigen Wasserstoffverbindungen zu erklären. H_2Se ist stabil und bildet sich schneller (vergleich auch Tab. 1) und wirkt somit auf die Te-AA stark depressiv. Andererseits wird die Se-AA von der Tellur-Matrix aus dem gleichen Grund weniger beeinflußt.[19,20]

Die gefundenen Ergebnisse stimmen nur zum Teil mit denen der Literatur überein.[19–21] Es muß allerdings bei dieser Einschätzung berücksichtigt werden, daß sich die Literaturangaben auf die Hydriderzeugung in Verbindung mit der Flammenatomisierung beziehen. Oftmals wurden auch ganz andere Ionen auf ihren Einfluß getestet, z.B. finden Pierce und Brown,[21] daß Cd^{2+}- und Sr^{2+}-Ionen eine stark depressive Wirkung besitzen. Danach folgen Co^{2+}, Cu^{2+}, Ag^{+} und Sn^{2+}-Ionen. Dieses Verhalten ließe sich mit der Bildung von schwerlöslichen Seleniden bzw. Selenaten (Sr) erklären. Allerdings wird davon berichtet, daß beim vorherigen Ansäuern der Probelösung die Matrixeffekte der Kationen verschwinden. Dieses Ergebnis kann von uns nicht bestätigt werden.

Tabelle 3. Übersicht über die möglichen Ursachen der Matrixeffekte bei Anwendung der direkten elektrothermischen Atomisierung in der Graphitrohrküvette

Art des Einflusses	Matrices P	Sb	As	Bi	Ga	In	Ge	Te	Sn
A. Signaldepression									
1. Bildung schwerflüchtiger Verbindungen	–	(+)	–	(+)	(+)	(+)	(+)	–	(+)
2. Verdampfung der Spur mit einer leicht flüchtigen Matrix	–	–	(+)	–	–	(+)	–	+	–
3. Molekülbildung zwischen Matrix und Spur im Plasma	–	+	–	+	–	–	+	+	+
B. Signalerhöhung									
1. Bildung schwerflüchtiger Verbindungen	–	(+)	–	(+)	(+)	(+)	(+)	–	(+)
C. Vergrößerung der Intensität des Untergrundes									
1. Streulicht bei gleichzeitiger Verdampfung von Spur und Matrix	+	–	–	(+)	+	+	+	+	+

+ Einfluß vorhanden, (+) Einfluß möglicherweise vorhanden, – kein Einfluß.

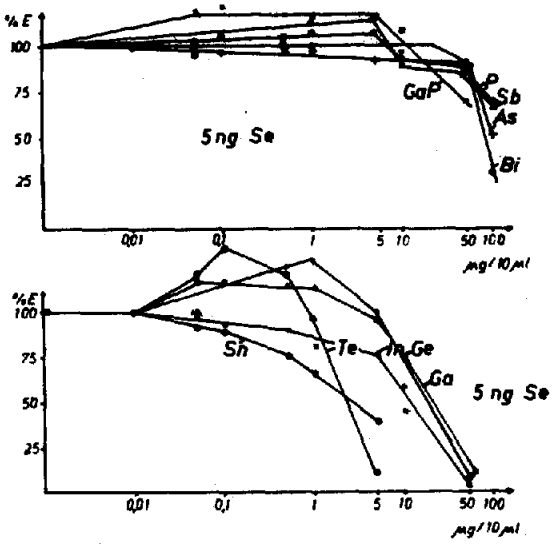

Abb. 5. Abhängigkeit der Se-AA von der Gegenwart anorganischer Matrices bei Einsatz der direkten elektrothermischen Atomisierung in der Graphitrohrküvette.

Robert[20] und Smith[19] testeten ebenfalls nicht den Einfluß hydridbildender Matrices. Auch aus ihren Ergebnisse geht hervor, daß der Einfluß durch die Bildung schwerlöslicher Verbindungen die Priorität besitzt.

Im Ergebnis dieser Untersuchungen muß festgestellt werden, daß die durch die Hydridmethode angestrebten chemischen Spur–Matrix-Trennungen nur bedingt realisierbar sind.

Elektrothermische Atomisierung

In der Tabelle 3 wurde wiederum versucht, eine Übersicht über die möglichen Matrixeffekte bei der Se- bzw. Te-AA beim Einsatz einer Graphitrohrküvette zu geben. Es kann eingeschätzt werden, daß gegenüber der Hydridmethode besonders der Streulichtanteil erheblich ansteigt. Außerdem sollte auch die Molekülbildung zwischen der Spur und Bestandteilen der Matrix im Plasma infolge der durch die gleichzeitige Verdampfung bedingten hohen Konzentration stark zunehmen. Spezielle Untersuchungen der Molekülabsorption mit Hilfe einer Wasserstoffhohlkathodenlampe (Kontinuum) beim Einsatz hoher Se- und Matrixmengen zeigten, daß folgende Moleküle im Plasma der Graphitrohrküvette existieren: BiSe (190–230 nm, 270–280 nm); SbSe (330–340 nm, 220–225 nm); GeSe (230–320 nm); SnSe (190–220 nm); TeSe (220–230 nm). Die angegebenen Werte charakterisieren die gefundenen Absorptionsbanden.

Die Mehrzahl der übrigen Matrixeffekte ist jedoch nicht eindeutig bestimmbar, so daß in diesem Fall auch keine Reihenfolge der Elemente hinsichtlich ihres Matrixeinflusses ableitbar ist.

In der Abbildung 5 sind die experimentellen Ergebnisse, die bei der Untersuchung des Matrixeinflusses auf die Se-AA erhalten wurden, angegeben. Bei der Auswertung dieser Ergebnisse kann man 2 Gruppen der Elemente bilden:

1. Gruppe: GaP, P, Sb, As, Bi mit geringem Einfluß;
2. Gruppe: Ga, Ge, In, Te, Sn mit größerem Einfluß.

Gegenüber der Hydridmethode ist festzustellen, daß der Matrixeinfluß bei der Anwendung der Graphitrohrküvette im allgemeinen größer ist.

Der geringere Einfluß der in der ersten Gruppe genannten Substanzen ist vor allem darauf zurückzuführen, daß thermische Matrix–Spur-Trennungen zum Teil möglich sind. Dadurch wird die Konzentration der Matrix während der Atomisierungsphase im Plasma reduziert. In allen anderen Fällen führte die Optimierung der thermischen Bedingungen zu keiner Spur–Matrix- oder Matrix–Spur-Trennung. Weitere Detailuntersuchungen zur Klärung der einzelnen Einflüsse wurden nicht durchgeführt.

ERGEBNISSE DER ANALYTISCHEN BESTIMMUNG VON Se UND Te DURCH AA IN GEGENWART ANORGANISCHER MATRICES

In der Tabelle 4 sind die analytischen Ergebnisse zusammengefaßt worden, wodurch auch eine Einschätzung der Anwendbarkeit der beiden Atomisierungstechniken möglich ist.

Die ersten beiden Säulen der Tabelle weisen aus, daß bei Einsatz der Hydridmethode in Gegenwart von Ga, P (als PO_4^{3-}) und GaP (als Ga^{3+}/PO_4^{3-}) Spurenbestimmungen des Selen und Tellur im ng/g- bis µg/g-Bereich (bezogen auf die Masse der anorganischen Matrices) möglich sind. Die relativen Nachweisgrenzen in Gegenwart von Te (als TeO_3^{2-}), In, Bi und Ge (als GeO_4^{4-}) von 10^{-2} bis 10^{-3}% lassen keine extremen Spurenbestimmungen zu. In Gegenwart von Arsen, Antimon, Zinn und Selen sind nur Bestimmungen im Prozent-oder Promille-Bereich möglich. Bei Anwendung der elektrothermischen Atomisierung in einer Graphitrohrküvette liegen die relativen Nachweisgrenzen in Gegenwart der meisten anorganischen Matrices zwischen 10^{-2} und 10^{-3}%. Das bedeutet, daß in keinem Fall eine extreme Spurenbestimmung möglich ist. Diese Tatsache resultiert aus dem durchschnittlich stärkeren Matrixeinfluß. Auf den ersten Blick erscheint somit die Hydridmethode in vielen Fällen günstiger. Allerdings ist bei dieser Bewertung auch zu berücksichtigen, daß bei der Untersuchung vollständig unbekannter Proben mit der Hydridmethode falsche Ergebnisse erhalten werden können, weil der Einfluß der einzelnen Matrices sich sehr stark voneinander unterscheidet. Beim Vergleich der relativen Nachweisgrenzen beider Atomisierungstechniken kann man hinsichtlich der Anwendbarkeit der Methoden 3 Gruppen von Matrices unterscheiden.

1. Ga, GaP, P: Hydridmethode ist besser.

Tabelle 4. Möglichkeiten für die Bestimmung des Selen und Tellur in Gegenwart anorganischer Matrices durch AAS bei Anwendung unterschiedlicher Atomisierungstechniken

Matrix	Nachweisgrenzen bei Anwendung der Hydridmethode, *ppm*		Graphitrohrküvette, *ppm*		Verhältnis der Nachweisgrenzen	
	Se	Te	Se	Te	Se	Te
Ga	0,02	0,2	50	6	5.10^3	30
P	0,1	0,2	5	13	5.10^2	65
GaP	0,1	0,5	10	5	10^2	10
Te	10	—	10^2	—	10	—
In	10	20	50	—	5	—
Bi	10	—	10	—	1	—
Ge	10^2	80	50	—	0,5	—
As	10^2	2.10^3	10	5	0,1	0,003
Sn	10^4	—	10^2	—	0,01	—
Sb	10^4	2.10^3	5	—	0,0005	—
Se	—	2.10^3	—	—	—	—

2. Te, In, Bi, Ge: Beide Methoden sind vergleichbar.

3. As, Sn, Sb: Elektrothermische Atomisierung in der Graphitrohrküvette ist besser.

Somit kann festgestellt werden, daß der Einsatz der einen oder anderen Technik immer nur in Abhängigkeit vom analytischen Problem angegeben werden kann.

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Summary—The determination of traces of Se and Te by AAS with generation of volatile hydrides and atomization in a quartz tube, and by AAS with direct electrothermal atomization in a graphite cuvette, is described. The instrumental parameters and the experimental conditions were optimized. For pure acidic solutions it was found best to determine selenium by the hydride technique and tellurium by direct electrothermal atomization. The influence of $A^{III}B^{V}$-matrices, and of other substances which also form volatile hydrides, on the determination of Se and Te was investigated. When the hydride technique was used it was found that the main causes of the depression of the AA signals are the formation of insoluble compounds between the matrix and H_2Se or H_2Te, and the loss of $NaBH_4$ by reaction with reducible compounds. In the case of the graphite cuvette the formation of stable molecules in the plasma and increased light-scattering are the main causes of interference. The analytical possibilities of the methods are compared and the advantages and disadvantages are described.

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DETERMINATION OF SMALL CONCENTRATIONS OF HCl BY DERIVATIVE FORMATION—A PROBLEM AND HOW IT MIGHT BE SOLVED

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Summary—In the investigation of methods for the determination of chloride three reactions for making derivatives of HCl have been developed. The individual problems which arise for the different methods are discussed. The reactions are reaction of CrO_3 with HCl to give CrO_2Cl_2, reaction of epoxides with HCl to produce α-chloro-alcohols and reaction of $C_6H_5HgNO_3$ with HCl to form C_6H_5HgCl. The detection methods used are γ-spectrometric measurement of ^{51}Cr-labelled CrO_2Cl_2, gas-chromatographic determination of α-chloro-alcohols with flame-ionization, electron-capture or electrolytic-conductivity detectors and the determination of C_6H_5HgCl by AAS.

The determination of HCl or Cl^- in low concentrations is difficult for a number of reasons; the problems arise partly in sampling owing to the polarity of HCl (Cl^-). The adsorption losses are high and all container walls or substances involved in the sampling procedure or separation process are contaminated with chloride.

The second problem is the difficulty of spectroscopic measurement of Cl, by atomic-absorption spectroscopy for example. Owing to the problem of detection as well as of adsorption losses all determinations of HCl involve indirect methods.

We are engaged in the investigation of reactions of chloride or hydrogen chloride with the aim of finding indirect methods for the determination of chloride through preparation of derivatives. The selection of suitable compounds for reaction with HCl depends on the separation and detection method selected. The application of reactions of HCl (Cl^-) with the aim of an indirect detection demands the observation of several conditions for preparation of the derivative and for the detection, just as several demands have to be fulfilled by the separation method. Generally the detection methods should be suitable for the selected conditions and methods of reaction and separation.

This paper does not present final results but is intended to demonstrate (for different examples) the difficulties due to the chemical reactions and the separation and detection methods.

ANALYTICAL REQUIREMENTS

Derivative-formation methods

The reaction rate must be sufficiently high for equilibrium to be reached within an acceptable time. The equilibrium should be such that a quantitative reaction is obtained even at small concentrations of HCl. The chemical properties of the reagent and the reaction product should be sufficiently different to enable a quantitative separation to be made. The reagents and solvents used should be extremely pure and readily purifiable, and should contain as little chloride as possible (preferably none).

Separation methods

The separation method must be capable of separating the reaction product (which is to be determined) from all interfering compounds. No steps which introduce interfering impurities should be included in the separation procedure. The separation method has to be fast and easy to handle.

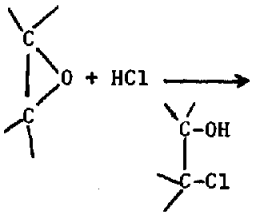
Detection methods

The detection limit for the reaction product has to be low enough for the analytical problem to be solved. Taking into account the efficiency of the chosen separation method, the detection should be sufficiently selective. The calibration graphs for the compounds which are to be determined should be linear in the range of interest and the detection method has to be fast and easy to handle.

An indirect analytical method which fulfils all these requirements is possible only in exceptional cases. For practical analytical applications it is necessary to distinguish between conditions which must be fulfilled and those requirements which are merely desirable.

The weight given to the different points in detail depends on the practical analytical problem. Undoubtedly the three steps, derivative formation, separation and detection, should provide a suitable analytical procedure in the chosen combination. In the following section we have attempted to discuss these problems for the analytical methods of indirect deter-

Table 1. Examples of indirect detection methods for chloride

Reactions	Separation methods	Detection methods
$*CrO_3 + HCl \longrightarrow *CrO_2Cl_2$	Volatilization	Radioactivity measurement (AAS)
$C_6H_5HgNO_3 + HCl \longrightarrow C_6H_5HgCl$	Extraction (gas chromatography)	AAS (FID, ECD, radioactivity measurement)
	Gas chromatography	FID, ECD, ElCD (electrolytic conductivity detector)

mination of chloride which we have developed and tested. These indirect detection methods are summarized in Table 1.

POSSIBLE METHODS

Determination with CrO_3

One of the possibilities for the detection of HCl is its reaction with a solid compound and the formation of a volatile product.

$$A(solid) + HCl(gas) \rightarrow B(volatile)$$

This general reaction scheme is best fulfilled by the formation of volatile oxychlorides from non-volatile metal oxides. Taking into consideration the remarks made in the introduction the following reaction seems to be very promising:

$$CrO_3 + 2HCl \rightleftharpoons CrO_2Cl_2 + H_2O$$

The reaction takes place at 110–150°. The CrO_2Cl_2 formed is transported at 200° to a decomposition zone (second detection position) at a temperature of 700° (Fig. 1). At this temperature CrO_2Cl_2 decomposes to give Cr_2O_3. The alternative of collecting CrO_2Cl_2 by condensation at −50° is not feasible because trace amounts of CrO_2Cl_2 are too volatile for collection to be complete. Also residual HCl may be condensed together with the CrO_2Cl_2 at such low temperatures. The principle of this analysis is the proportionality between transported Cr and HCl. The transported chromium can be detected by several methods.

We have used γ-spectrometric measurement by labelling the CrO_3 with ^{51}Cr. The detection limit depends on the specific activity of CrO_3, the chemical state and vapour pressure of the CrO_3 after irradiation, and side-reactions.

For the development of this method the application of radioactive tracing is preferred, since the reaction of HCl with CrO_3 can be followed easily as a function of all parameters except chemical behaviour. In principle the deposited Cr can also be measured, for

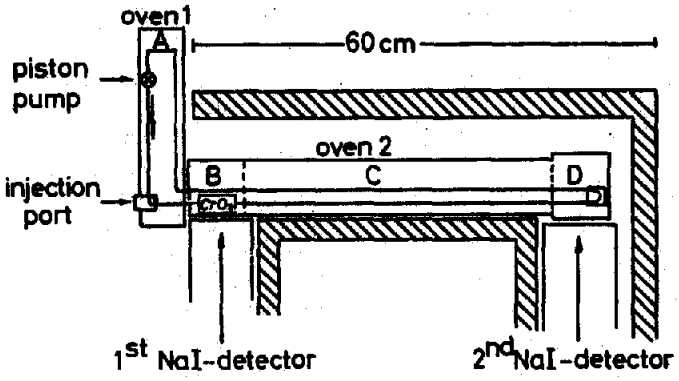


Fig. 1. Schematic design of the apparatus for the derivative-formation reaction of HCl with CrO_3. A, injection port and pumping zone at 70°C; B, reaction zone for CrO_3 at 150°C; C, transportation zone at 200°C; D, condensation zone with packing of quartz granules, at 700°C. Quartz tubing, o.d. 4 mm, bore 2 mm.

example, by the use of AAS with a graphite-furnace atomizer, and in this case the theoretical detection limit is 10 pg of Cr, corresponding to 14 pg of Cl.[1] If CrO_3 activated by thermal neutrons is used, the theoretical detection limit in our experiments is 1 ng of HCl, owing to the low specific activity of the ^{51}Cr formed. This can be considerably improved by using carrier-free ^{48}Cr, which is commercially available.

Unfortunately a number of interferences have to be taken into account when HCl reacts with CrO_3. These are the adsorption of HCl on the walls of the apparatus, the possibilities of consecutive and side-reactions of CrO_3 (Fig. 2), the reaction of HCl with the decomposition and reduction products of CrO_3, the influence of water on the equilibrium of the reaction between CrO_3 and HCl, and changes in the surface of the CrO_3 after irradiation.

The adsorption of HCl on the walls is reduced by heating the apparatus to 200°. By passage of HCl over CrO_3 several times in a cyclic process the yield of CrO_2Cl_2 is increased. Unfortunately the reaction is not complete, owing to H_2O which is formed in this reaction but not removed. (It should be considered whether a method is suitable for the determination of HCl if even traces of H_2O have to be excluded.) The heterogeneous reaction of CrO_3 with HCl is an example of a reaction which at first sight seems elegant and simple but later reveals numerous problems which have to be solved.

Determination with $C_6H_5HgNO_3$

The product of the reaction of $C_6H_5HgNO_3$ with HCl is C_6H_5HgCl. The reagent and the product may be separated by solvent extraction. The detection method is gas chromatography[1,2] or AAS.[3,4] At present we use the detection of mercury by AAS (with a graphite-furnace atomizer) for the indirect detection of chloride. The reaction of HCl with $C_6H_5HgNO_3$ is fast and complete. The C_6H_5HgCl formed is soluble in organic solvents, being covalent. Because $C_6H_5HgNO_3$ has almost the same solubility in acid solution as in organic solvents, the organic layer has to be scrubbed with 0.1*M* nitric acid in order to achieve a good separation between $C_6H_5HgNO_3$ and C_6H_5HgCl. This step is not necessary if gas chromatography is used as the separation and detection method, but the detection of chloride is faster by AAS than by gas chromatography.

The theoretical detection limit for C_6H_5HgCl which can be reached at the present time with a graphite-furnace atomizer corresponds to 2 pg of an injected volume of 10 µl. The amount which can be measured with sufficient accuracy is about 4 pg. The theoretical limits for gas chromatographic detection with an ECD are in the same range.[1,2,5] The extraction step could lead to the possibility of enrichment by evaporation of the solvent. Extraction of larger volumes and subsequent concentration gives better reproducibility and reduces handling problems.

Another method is the γ-spectrometric detection of ^{203}Hg, by employing labelled $C_6H_5HgNO_3$. The separation step is also extraction. With a specific activity of 10 µCi/100 µg of ^{203}Hg, 100 pg of C_6H_5HgCl can be detected, corresponding to 10 pg of Cl. With greater care in the measurement and by use of $C_6H_5HgNO_3$ having a higher specific activity, this value should be improved. In this range the effect of impurities (Cl-content of chemicals and solvents) determines the detection limit.

Determination with epoxides

The products from the reaction of epoxides with HCl are α-chloro-alcohols. For these compounds a

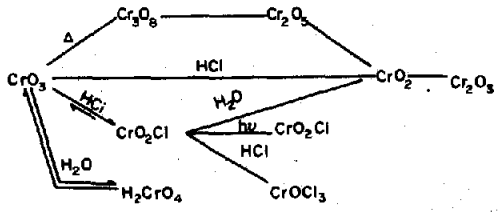


Fig. 2. Side-reactions and consecutive reactions in the system CrO_3–HCl.

suitable separation and detection method is gas chromatography, with sensitive detectors (flame-ionization,electron-capture,electrolytic-conductivity or flame-photometric). We have used the first three for the detection of the α-chloro-alcohols. They possess different detection sensitivities and selectivities for different compounds. The flame-ionization detector (FID) is sensitive to compounds containing carbon atoms or C–H bonds and has limited specificity. The electron-capture detector (ECD) is very sensitive and is specific for compounds containing halogen atoms or nitro groups (or other electron-attracting groups). The electrolytic-conductivity detector (ElCD) has a high detection sensitivity for substances contributing to a conductivity change in the electrolytic measuring cell, after pyrolysis in the presence of hydrogen.

For detection with an ECD, epoxides with electron-attracting groups seem very suitable, because the halogenated products can be detected with high sensitivity. Epoxides with electron-attracting groups, however, react only slowly with HCl and some of them form unstable reaction products (*e.g.*, 1-chloro-3-iodopropanol). To attain a reaction rate as high as possible, unsubstituted epoxides must be used. For example, the reaction of HCl with ethylene oxide is fast,[6] but problems arise in the handling and measuring out of the reagent. A compromise between fast reaction, simple handling and high detection sensitivity is obtained with cyclohexene oxide [7-oxabicyclo-(4,1,0)-heptane]. If an FID is used, a theoretical detection limit corresponding to 2 pg of HCl is reached with a capillary column, or 100 pg of HCl with a packed column.[7]

We have also investigated the possibility of using epichloro-, bromo- and iodohydrins as reagents for HCl, because the reaction products have low detection limits if an ECD is used. The reaction rate of the halogen-substituted epoxides[8] with HCl decreases in the sequence Cl > Br > I, as do the stabilities of the original compounds. With a capillary column the theoretical detection limits (corresponding to HCl) for the reaction products of the substituted epoxides are 1,3-dichloropropanol, 2 ng of HCl,[9] 1-chloro-3-bromopropanol, 8 pg of HCl and 1-chloro-3-iodopropanol, 0.4 pg of HCl.[8]

For very small quantities of HCl (in the nanogram range) however, the reaction times are so long that the detection of HCl with these substances is not practicable.

A general problem encountered with derivative-formation reactions is that one reaction partner (HCl) is present at low concentration, thus lowering the reaction rate. To keep the reaction rate sufficiently high the other reactant has to be present in very large excess. A further possibility of increasing the reaction rate is the use of elevated temperatures, but this may not be appropriate in all cases. We have also used an ELCD as gas-chromatographic detector for the determination of 2-chlorocyclohexanol (reaction product of cyclohexene oxide and HCl). It may be considered surprising that derivative-formation is recommended for the detection of HCl by conductivity measurement, but the reason is quite simple. For determination with an ElCD, HCl must be separated from other substances which could contribute to a change in conductivity. Conventional gas chromatographic columns which could be used for the separation of HCl from other compounds are not suitable for the detection of very small quantities of chloride, because of the high adsorption losses. Hence derivative formation is used to facilitate a quantitative separation, but this does not directly lower the detection limit. However, the detection limit can be lowered indirectly by the separation from interfering substances. The advantage of the ElCD is its selectivity for compounds which contribute to conductivity after pyrolysis in the presence of hydrogen. This diminishes interferences from many impurities and thus reduces the requirements for separation. It is possible to provide calibration for other methods by use of the ElCD, because the source of the HCl standards (*e.g.*, a permeation tube or desorption tube) can be connected directly to the ElCD. The disadvantages of this detector are that the detection limit (5 pg of HCl) is higher than that for an FID, and the detector is more difficult to operate and more expensive. Most gas chromatographs are nowadays equipped with an FID, but very few with an ElCD. We think that a comparison of the three chromatographic detectors shows that the FID is the most suitable for the determination of HCl by derivative formation with epoxides.

The method has the advantage, however, that it can be used in any analytical laboratory equipped with a modern gas chromatograph, without the need for any additional expensive equipment.

The detection limits of these methods are in the range of 4 ppM (parts per milliard). When an enrichment step is used (*e.g.*, cryogenic sampling of air; extraction from liquid samples) the final volume which can be separated by gas chromatography plays an important role in the detection of small quantities. On a capillary column the maximum sample volume is 0.1 μl; on packed columns (depending on the diameter) sample volumes up to 10 μl may be used. This means that the maximum quantity which can be separated on a packed column is up to one hundred times that which can be separated on a capillary column. The detection limit for HCl is 100 pg with packed columns (if cyclohexene oxide is used as derivative-formation reagent), but is 2 pg with capillary columns, so, if the difference in sample volume is taken into consideration, the detectable concentration is smaller by only a factor of two for packed columns, compared with capillary columns.

On the other hand, the separation efficiency of a capillary column is higher than that of a packed column, so the separation from interfering impurities is more efficient. Because the sample volume which can be used for the separation is very small in both

cases, to avoid loss in detection sensitivity because of dilution it is important to carry out the reactions in as small a volume as possible. At present we are not able to solve the problems of handling volumes much smaller than 50 μl.

Possible solutions to these problems are the evaporation of solvent before separation and coupling of a packed column of large capacity with a capillary column of high separation efficiency. Both solutions require considerable experimental effort and are very time-consuming, so are only recommended for extremely small traces of HCl.

Another possibility of increasing the detection sensitivity is the combination of the fast reaction of the unsubstituted epoxides with HCl and the high sensitivity of an ECD. To achieve this, HCl is reacted with but-1-ene oxide and the resulting 2-chloro-1-butanol is heptafluorobutyrylimidazole (HFBI) converted into its derivative,[10,11] thus introducing groups with a high electron-capture cross-section.[12] This method also involves considerable experimental effort and introduces new problems (additional separations for example).

CONCLUSION

The theoretical detection limits for the derivative-formation methods are extremely low, and correspond to concentrations in the ppM-range or quantities at the picogram level. At the present time, however, owing to various problems (reaction rate, sample volume, impurities, interferences) we are not able to determine HCl in concentrations lower than 0.1 ppm (corresponding to several ng of HCl). Future investigations will deal with the problem of getting closer to the theoretical detection limits. The different methods investigated so far present a choice of method for any specific problem. If more than one method can be used for detection of chloride, the results can be compared.

The derivative-formation methods presented here are suitable for the detection of small traces of chloride, but they are all expensive in some way or other and should only be employed if very small traces have to be detected.

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VERTEILUNGSVERHALTEN EINIGER DIETHYLDITHIOPHOSPHINATOCHELATE: ANWENDUNG ZUR GASCHROMATOGRAPHISCHEN BESTIMMUNG DES CADMIUMS

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Zusammenfassung—Das Verteilungsverhalten der Diethyldithiophosphinate des Cadmium, Zink, Nickel, Kobalt und Blei werden für das System Wasser/Toluol (Chloroform) gaschromatographisch bestimmt. Die gaschromatographische Bestimmung des Cadmium als Diethyldithiophosphinatochelat im Bereich von 0,03 bis 0,3 ppm Cd in wässriger Lösung wird beschrieben.

Die Diethyldithiophosphinatochelate einiger Metalle lassen sich aus wässrigen Lösungen ausschütteln und spektralphotometrisch bestimmen.[1,2] Wegen ihrer hohen Flüchtigkeit und thermischen Stabilität sind sie auch gaschromatographisch zu analysieren.[3,4] In dieser Arbeit wird das Verteilungsverhalten der Diethyldithiophosphinate von Cadmium, Zink, Blei, Kobalt und Nickel in Abhängigkeit vom pH-Wert untersucht und eine Anwendung zur gaschromatographischen Bestimmung des Cadmiums beschrieben.

EXPERIMENTELLER TEIL

Die gaschromatographischen Untersuchungen werden mit einem Gaschromatograph Fractovap Serie 450, Modell GI (Fa. Carlo Erba) durchgeführt. Detektor: FID Typ 20. Es werden ausschließlich Glassäulen verwendet, die, um eine Zersetzung der Chelate am blanken Metall zu vermeiden, weit in die Eingangsöffnung des Einspritzblocks hineintragen. Die Probe kann somit praktisch direkt in die Säule eingebracht werden. Alle benutzten Lösungsmittel und Chemikalien sind p.a., die Lösungen werden mit bidestilliertem Wasser angesetzt. Zur Darstellung des Chelatbildners vgl. Citat 5. Die Metallchelate (Diethyldithiophosphinato = DEDTP) werden daraus durch einfachen Umsatz in wässriger oder alkoholischer Lösung (Co-Verb.) mit einem Überschuß des Metallsalzes hergestellt[6,7] und durch Umkristallisieren gereinigt. Zur Bestimmung des Verteilungsverhaltens werden die Chelate in der organischen Phase gaschromatographisch bestimmt. Eichkurven werden durch Einwaage reiner Chelate im jeweiligen Lösungsmittel aufgestellt. Die wässrige Phase wird zuvor mit dem organischen Lösungsmittel gesättigt. Es werden folgende Puffer benutzt: Kaliumbiphthalat-Puffer[8] (pH 3–6), Puffer nach Theorell und Stenhagen[8] (Citrat/Phosphat-Puffer), Borat-Puffer[8] (pH 7,7–8,5), Puffer nach Thiel, Schultz und Koch[9] (Borsäure/Bernsteinsäure-Puffer) (pH 3–8), Essigsäure/Acetat-Puffer.

® Die vorliegenden Untersuchungen wurden in dankenswerter Weise durch Mittel des Verbandes der Chemischen Industrie und der Deutschen Forschungsgemeinschaft ermöglicht.

ERGEBNISSE

Das Verteilungsverhalten einiger Diethyldithiophosphinatochelate

Als Lösungsmittel wird Toluol gewählt, in einigen Fällen auch Chloroform. Die gaschromatographischen Bedingungen bei den Verteilungsuntersuchungen sind: Säule GE SE 30,55% auf Chromosorb Q, 600 × 2,5 mm. Säule/Einspritzblocktemperatur: 220°/250°, beim Zink–Chelat 200°/245°. Das Verteilungsverhalten wird mit Metallkonzentrationen von 1 bis 1,5 mg/ml und einem drei-, beim Zink vier- und beim Nickel zehnfachen Reagenzüberschuß ermittelt. Das Volumenverhältnis ($=\gamma$) wässriger/organischer Phase ist eins.

Die zur Einstellung der pH-Bereiche benutzten Puffer werden angegeben. Sie können über die maskierende Wirkung ihrer Bestandteile das Verteilungsverhalten beeinflussen.

Zink. Puffer: Kaliumbiphthalat (a); Borat (b); Puffernach Theorell und Stenhagen (c); nach Thiel, Schultz und Koch (d). Die Ergebnisse der Verteilungsversuche zeigt Abb. 1. Bei Zugabe der Zinklösung zur gepufferten Lösung des Komplexbildners erfolgt keine sichtbare Ausfällung des Zinkchelats. Die Extrahierbarkeit wird offensichtlich stark von den Pufferbestandteilen beeinflußt. Ein Bernsteinsäure–Borsäure-Puffer (Thiel, Schultz und Koch) gibt die besten Ergebnisse. Versuche mit Chloroform als Lösungsmittel und einem Essigsäure–Acetat-Puffer ergeben einen ähnlichen Verlauf wie mit Puffer (d). Geht man zu größeren γ-Werten und zu kleineren Zink-Konzentrationen über, so verschlechtert sich die Ausbeute beim Ausschütteln des Zinks. Auch durch Mehrfachextraktion ist keine vollständige Extraktion mehr möglich. Erst bei größeren Zink-Konzentrationen (über 1–2 ppm) erhält man auch mit $\gamma = 10$ durch Mehrfachextraktion eine nahezu vollständige Extraktion des Zinkchelats, so daß die Aufstellung einer Eichkurve

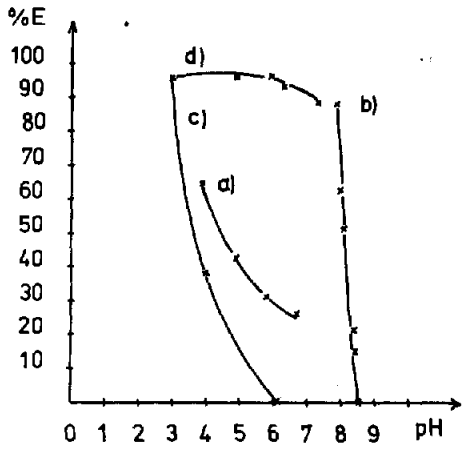

Abb. 1. Verteilungsverhalten des Zn–DEDTP (s. Text).

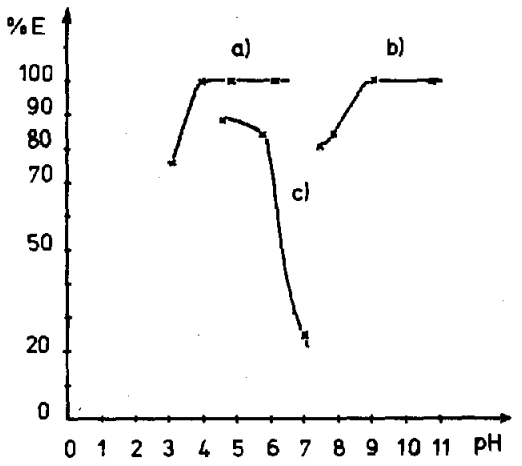

Abb. 3. Verteilungsverhalten des Pb–DEDTP (s. Text).

nach folgender Arbeitsvorschrift möglich wird. Zwanzig ml der zu bestimmenden Zinklösung (mit über 2 ppm Zn) wird zur Entfernung organischer Verunreinigungen und zur Sättigung mit Lösungsmittel mehrmals mit Chloroform ausgeschüttelt. Anschließend wird ein auf die höchste Metallkonzentration bezogener zehnfacher Chelatbildnerüberschuß zugesetzt und mit 2 ml Chloroform ausgeschüttelt. Das Ausschütteln wird noch zweimal mit je 1 ml des Lösungsmittels wiederholt. Die vereinigten Extrakte werden gaschromatographisch bestimmt. Die Bestimmung des Zinks ist neben einem wenigstens zehnfachen Überschuß an Blei, Cadmium und Nickel möglich. Neben Magnesium-, Calcium- und Phosphat-Ionen ist die Bestimmung des Zinks bei pH 3 in einem Puffer nach Theorell und Stenhagen (s.o.) ebenfalls möglich.

Cadmium. Puffer: pH 3–6 Kaliumbiphthalat; pH 7,8–11 Borat; pH 3–9 nach Theorell und Stenhagen. Die Ergebnisse zeigt Abb. 2. Im Gegensatz zum Zink fällt das Cadmium unter den Versuchsbedingungen als weißer Niederschlag aus. Der optimale pH-Bereich liegt zwischen 4 und 8, in dem Cadmium zwischen 96 und 98% im organischen Extrakt wiedergefunden werden kann, was innerhalb der Meßfehler praktisch vollständige Extraktion bedeutet. Mit Chloroform und einem Acetatpuffer ist Cadmium im pH-Bereich 3–6 ebenfalls praktisch vollständig extrahierbar. Mehrfachextraktionen mit $\gamma = 10$, einem hundertfachen Reagenzüberschuß und Chloroform als organische Phase ergeben mit Cadmiumkonzentrationen von 0,6 ppm bei bereits einmaligem Ausschütteln vollständige Extraktion des Chelats.

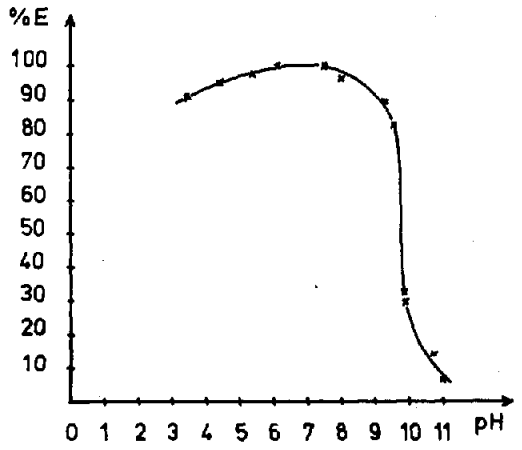

Abb. 2. Verteilungsverhalten des Cd–DEDTP (s. Text).

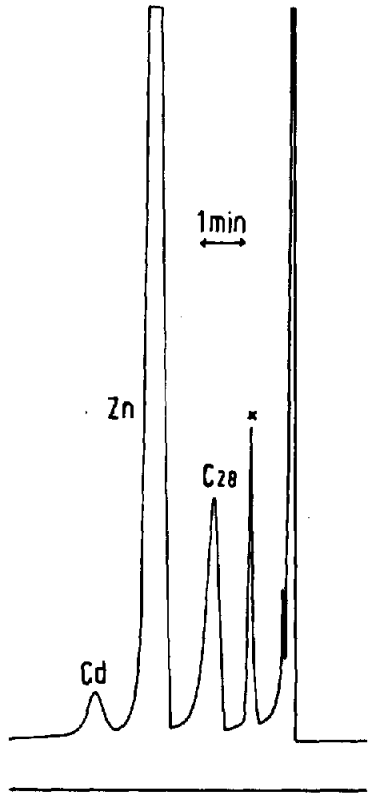

Abb. 4. Bestimmung des Cadmiums neben einem 100-fachen Zink Überschuß (0,06 ppm Cd, sonst. s. Text, * = Verunreinigung des Reagenz).

Tabelle 1. Gaschromatographisches Verhalten der Diethyldithiophosphinatochelate des Zink, Cadmium und Nickel

Säule	Temperatur, °C Säule–Einspritzblock	Retentionszeit, *min* Zn–DEDTP	Cd–DEDTP	Ni–DEDTP	Auflösung *R* $R_{Cd/Zn}$	$R_{Ni/Cd}$	Bemerkungen
OV-210 (1%)	180–200	0,7	1,4	1,4	2,0	—	nur zwei Peaks
OV-210 (3%)	190–210	3,6*	4,4*	7,1	1,4	2,7	
OV-210 (10%)	205–255	4,5	6,0	9,1	1,9	2,9	
OV-101 (3%)	190–210	3,8*	5,7	6,4	1,3	1,1	
GE-SE 30 (3%)	200–220	1,1	1,8	1,8	2,6	—	nur zwei Peaks
GE-SE 30 (5%)	200–220	7,1*	9,9	11,2	1,3	0,7	
Dexsil (1%)	200–220	4,8*	5,9*	5,9	0,7	—	nur zwei Peaks

OV-u. Dexsil-Säulen: Chromsorb HPW, 100–120 mesh, GE-SE 30-Säulen: Gaschrom Q, 80–100 mesh.
* leichtes (tailing).
Isothermer Betrieb, 40 ml/min Reinststickstoff, FID, Säule: 600 × 2,5 mm, 0,1 μg Chelat/μl, 1 μl eingespritzt, Lösungsmittel: Chloroform.

Kobalt. Es konnte mit verschiedenen Puffern und Toluol als Lösungsmittel keine Verteilung des Kobalts in die organische Phase festgestellt werden. Wie beim Zink erfolgte keine sichtbare Chelatfällung in Lösung.

Nickel. Im pH-Bereich 3–4 ist mit Toluol als Lösungsmittel eine *ca.* 7% ige Extraktion festzustellen. Mit Chloroform und einem 10-fachen Ligandenüberschuß steigt die Extrahierbarkeit auf *ca.* 13%. Auch nach mehrmaliger Extraktion ist eine vollständige Abtrennung des Nickels durch Verteilung nicht möglich.

Blei. Puffer: Kaliumbiphthalat (a); Borat (b); nach Theorell und Stenhagen (c). Die Ergebnisse der Verteilungsuntersuchungen zeigt Abb. 3.

Abgesehen vom pH-Bereich 7–9 ist eine praktisch vollständige Extraktion des Bleichelats möglich. Die Verbindung ist lichtempfindlich, bei diffusem Tageslicht tritt bereits nach *ca.* 45 min eine Zersetzung zu 6% ein,[2] bei direktem Sonnenlicht erfolgt die Zersetzung erheblich schneller. Man arbeitet daher mit Schütteltrichtern aus braunem Glas und nimmt die Messungen möglichst schnell vor. Eine gaschromatographische Bestimmung des Bleis ist wegen der längeren Retentionszeiten des Pb–DEDTP[2] besser bei temperaturprogrammierten Arbeitem möglich.

Verteilungsverhalten des Liganden

Die freie Diethyldithiophosphinsäure ist im Vergleich etwa zur freien Diethyldithiocarbaminsäure außerordentlich beständig.[1,2] Das Natrium-Salz ist selbst in 15*N* Schwefelsäure wochenlang stabil. Bei den Verteilungsversuchen wurde festgestellt, daß besonders im Bereich pH 1–3 Peaks auftreten, die aber mit mehrfach gereinigten Präparaten kleiner werden. Ebenso verschwinden diese Peaks oberhalb pH 3. Je nach Verlauf der Präparation des Chelatbildners und nach Reinheit der Ausgangsprodukte können bei nicht ausreichend umkristallisierten Produkten Peaks in der Nähe der Lösungsmittel auftreten, die aber die gaschromatographische Bestimmung der Metallchelate nicht beeinträchtigen (vgl. Abb. 4).

Gaschromatographische Bestimmung der Chelate

Zur Optimierung der gaschromatographischen Bestimmung werden Lösungen die das Nickel-, Zink- und Cadmium-Chelat gleichzeitig enthalten eingespritzt. Die Ergebnisse mit verschiedenen Säulen enthält Tabelle 1.

Die Auflösung *R* wird nach Leibnitz und Struppe[10] als

$$R = 1{,}177(t_{R2} - t_{R1})/({}_1b_{0,5} + {}_2b_{0,5})$$

angegeben. Als optimale Säule wird für die weiteren Bestimmungen die OV 210 (10%) Säule beibehalten (600 × 2,5 mm). Gaschromatographische Eichkurven für Lösungen dieser Chelate in verschiedenen Lösungsmittel (Chloroform, Toluol, 1,1-Dichloräthan, Tetrachlorkohlenstoff) waren im Bereich 30–1000 μg

Chelat/ml linear. Beim Sättigen der Lösungen des Zink-Chelats mit dem Komplexbildner (Natrium-Salz) konnte die Bestimmungsgrenze um das zehnfache erniedrigt werden. Die Reproduzierbarkeit der gaschromatographischen Bestimmung reiner Chelatlösungen ist je nach Spritzentyp, Einspritzvolumen und Auswerttechnik 1,5–9% (relative Standardabweichung aus 6–10 Einzelmessungen). Bei Auswertung gegen einen inneren Standard, hier der gesättigter Kohlenwasserstoff C_{28} (Fa. GC Accessories, Darmstadt), wird die Reproduzierbarkeit besser.

Die gaschromatographische Bestimmung sehr kleiner Metallmengen in wässriger Lösung nach Ausschütteln ihrer Diethyldithiophosphinatochelate ist nach obiger Darstellung für das Cadmium möglich.

Bestimmung des Cadmiums

Zehn ml der Lösung, die 0,03 bis 0,3 ppm Cd enthält und einen pH-Wert von 3–6 besitzt, wird mit 1 ml der Reagenzlösung (310 mg Natrium-Salz/25 ml) versetzt und driemal mit 1 ml Chloroform ausgeschüttelt (fünfmal bei Gehalten unter 0,1 ppm). Die Mehrfachextraktion gewährleistet auch ein sicheres Sammeln der mechanisch verteilten Tröpfchen der organischen Phase. Die organischen Extrakte werden anschließend bei 70° (Aluminium-Block) in geeigneten Glasgefäßen (vgl. Citat 11) eingedampft und mit 0,05 ml Chloroform, das 0,4 mg C_{28}/ml enthält, aufgenommen und davon 1 µl eingespritzt. Ausgewertet wird das Verhältnis Peakhöhe × Retentionzeit (Cd)/Peakhöhe × Retentionzeit (i.St.). Die Bestimmung des Cadmiums ist nach diesem Verfahren neben einem wenigsten 100-fachen Zinküberschuß möglich, wie Abb. 4 ausweist. Bei höheren Zinkkonzentrationen muß der Reagenzüberschuß entsprechend erhöht werden.

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Summary—The partition behaviour of the diethyldithiophosphinate chelates of Cd, Zn, Ni and Pb in the water/toluene (chloroform) system is investigated by gas chromatography. The determination of Cd as the diethyldithiophosphinate complex in aqueous solution in the range 0.03–0.3 ppm is described.

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IN SITU MICROANALYSIS OF IRON COMPOUNDS BY VALENCE-BAND X-RAY SPECTRA ON THE BASIS OF THE BAND VECTOR AND REPRESENTATIVE-SPACE TRANSFORMATION CONCEPT

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Summary—The band vector and representative-space transformation concept was applied to characterize the fine structure of Fe $L_{\alpha 1,2}$ (valence band) spectra of different iron compounds for their direct identification.

The direct identification of solids by evaluation of the fine structure of X-ray valence-band spectra has received considerable attention from physicists and analytical chemists.[1] If an electron beam is used for excitation of the X-ray signal then the analytical information arises from a volume which is a few μm in diameter and depth. This allows the microanalysis of a compound to be performed *in situ*.[2] The main limitations for the routine use of the direct identification of compounds or phases in a heterogeneous solid are the small differences in the fine structure of the X-ray spectra of the individual compounds, the loss of small (but characteristic) features in the spectral (statistical) noise, and the difficulties in recording the spectra and the measurement of their features with high accuracy and precision. In order to overcome these limitations, a concept for the analytical use of X-ray valence-band spectra has been proposed, based on the application of digital measurement techniques, mathematical smoothing (over suitable energy intervals), characterization of the spectral fine structure by means of a band vector and transformation of the information contained in the vector into two-dimensional space, thus allowing visual distinction between different compounds.[3] This approach has been tested with copper compounds. Most of the 14 compounds tested could be identified unequivocally on the basis of the evaluation of the Cu $L_{\alpha 1,2}$ line. It is the purpose of this paper to describe further applications of this technique. Iron compounds were chosen because the Fe $L_{\alpha 1,2}$ spectra are of interest in the determination of the oxidation state of Fe in oxides.[5–7] The evaluation of the Fe $L_{\alpha 1,2}$ spectra has been limited to this specific task, though the direct identification of the compounds (which is much more difficult) is important in the study of minerals, meteorites or other materials containing phases consisting of iron compounds. The separate steps involved in the analysis are discussed below.

Digital recording

In order to achieve high precision and accuracy in the measurement of the spectra a digital spectrometer scanning technique must be used. The high-resolution crystal spectrometer is operated in a stepwise manner with the aid of a computer. In this mode the wavelength increment between the individual points of measurement of the X-ray intensity can be kept sufficiently small and a high X-ray intensity at each wavelength can be maintained with a measurement time of a few seconds. The statistical noise is thus significantly reduced compared with that obtained by conventional analogue recording.[4]

In our experiments, an electron microprobe of the type ARL-SEMQ coupled with a PDP 11-05 computer was used. The wavelength region of interest was scanned with an RAP-crystal in wavelength increments of 0.000649 Å, or a multiple of this. The measurement time at each wavelength was either 2 or 4 sec, giving a total recording time for each spectrum of 10–20 min. The spectra (represented as intensity *vs.* wavelength) were punched on paper tape and processed further with a CDC CYBER 74 computer.

Figure 1 shows the computer-plot of the digitally recorded Fe $L_{\alpha 1,2}$ spectra of pure Fe and 8 different compounds (defined mineral phases). Although some characteristic features, such as the small peak-width for pure iron, pyrite and marcasite and the larger widths for the other compounds can be visualized, it is impossible to distinguish different compounds by visual comparison. Even if the parameters normally used for the characterization of spectra (wavelength

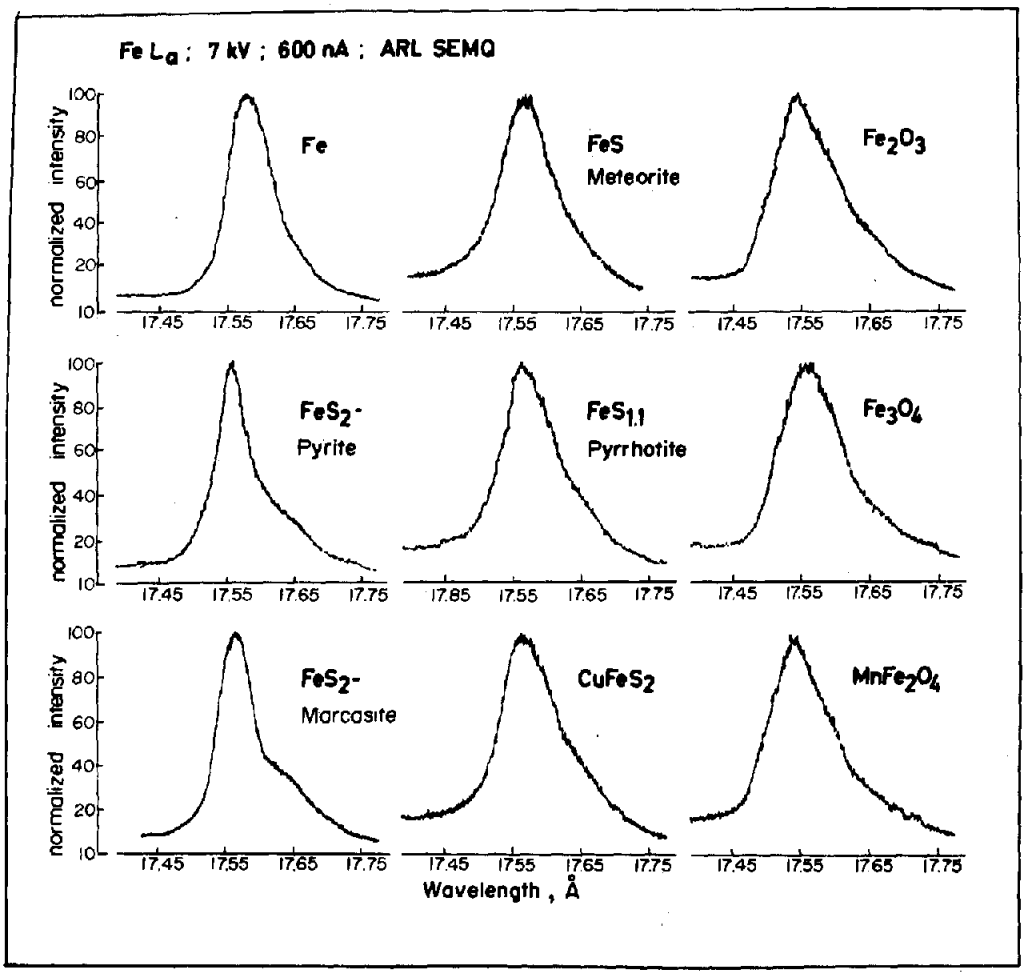

Fig. 1. Fe $L_{\alpha 1,2}$ Spectra of pure iron and iron compounds. Analytical conditions: electron microprobe analyser, ARL-SEMQ; excitation energy, 7 keV (in order to avoid interference by Fe K_α in 9th order); sample current 600 nA, Area scanning technique (30 × 30 μm); RAP-crystal; wavelength increment, 0.000649 Å; Measuring time per increment, 2 sec.

of intensity maximum, half-width and asymmetry number) were to be determined, the unequivocal identification of a compound on the basis of evaluation of its Fe $L_{\alpha 1,2}$ spectrum alone would not be possible.

Smoothing

The smoothing of the spectra serves to reduce the statistical fluctuations which determine the accuracy and precision of representation of the fine structure. The "Least Squares Polynomial Smoothing" algorithm of Savitzky and Golay[8] proved to be best suited for this purpose.[4] The effect achieved is that the error of determination of a spectral parameter is reduced by a factor which is equal to the square root of the number of wavelength increments (steps) over which the smoothing is carried out. Mathematical smoothing over, *e.g.*, 25 increments therefore corresponds to an improvement of the statistical error similar to that achieved by 5 repetitive measurements of the same spectrum. The problem associated with this procedure is that the smoothing interval must be accurately optimized according to the spectral resolution the features to be detected, in order to prevent the loss of information caused by using smoothing intervals that are too large.

Band vector

For accurate and precise characterization of the fine structure of a spectrum the function of intensity *vs.* peak-width can be used. This function is then represented by 8 or 9 points, each corresponding to the peak-width at intensities which are 10, 20 ... 90% of the maximum intensity. These values of the peak-width form a set of numbers which is characteristic of the structure of the spectrum and of the compound responsible for the X-ray line measured. This set of numbers can be represented by an 8- or 9-dimensional vector, which means that the spectrum is characterized by a point in 8- or 9-dimensional space. Spectra of different compounds showing differences

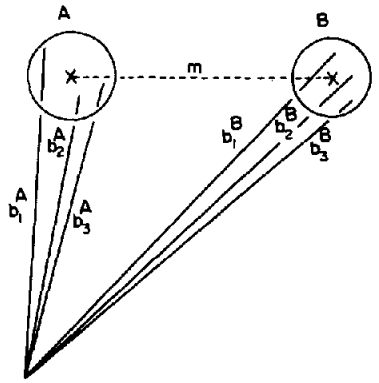

Fig. 2. Schematic representation of band vector concept. A, B, individual compounds; $b_i^{A,B}$, band vectors of compounds A and B; $i = 1, 2, 3 \ldots$ individual recordings of a spectrum; m, distance between the average values of the band vectors of compounds A and B.

in fine structure are located at different places in the space, the distance between points being characteristic of the differences in spectral structure. The repetitive recording of the spectrum of one compound leads to a cluster of points in vectorial space, the distance between the points being determined by the precision of the measurement of the spectral features (Fig. 2). The confidence interval of the determination of the features is thus represented by the diameter of a sphere which encompasses the cluster according to the statistical criteria defined. The relation between the diameter of the sphere and the distance between the centres of the spheres determines the statistically proved distinguishability of the spectra and as a consequence, of the compounds investigated. For the determination of the iron compounds, an 8-dimensional vector was used, given by the width of the Fe $L_{\alpha 1,2}$ peak at 20, 30, 40, 50, 60, 70, 80 and 90% of the maximum intensity. A lowest intensity value of 20% was chosen so that for all compounds the background intensity would be smaller.

Representative-space transformation

Although the representation of the structure of a spectrum by an 8- or 9-dimensional vector is suitable for the characterization of the compound, it has the disadvantage that it cannot be visualized. In order to visualize differences in the structure of the spectra and to distinguish between the compounds it is necessary to transform the information from 8- or 9-dimensional space into 2- or 3-dimensional space. This can be achieved without losing the characteristic information, *i.e.*, the diameter of the spheres (representing a spectrum) and the distance between the different spheres, by applying the concept of "Representative-Space Transformation", developed by Lin and Chen.[9]

The representative-space transformation is carried out by relating the spectral points in multidimensional space to a pair of auxiliary spectral functions and representing the ratios of the distances in, *e.g.*, 2-dimensional space. In 2-dimensional representation each spectrum is characterized by a point described by the co-ordinates p_1^* and p_2^*, which correspond to the average values of the spectral parameters, and by a circle, the diameter of which indicates the precision of the measurement. The distances between the circles represent the distinguishability.

More details about the application of the representative-space transformation concept for X-ray valence-band spectra are given in an earlier paper.[3] For the transformation of the 8-dimensional vectors representing the structure of the Fe $L_{\alpha 1,2}$ line into 2-dimensional space, pairs of Gauss, Lorenz and triangle functions were used as auxiliary functions. They were defined according to the criteria that the half-widths of the functions 0.13 and 0.07 Å, were slightly larger and smaller, respectively, than the half-widths of the Fe $L_{\alpha 1,2}$ lines.

Figure 3 contains the 2-dimensional representation of the Fe $L_{\alpha 1,2}$ spectra shown in Fig. 1. Each spectrum was recorded 5 times. The circles represent the 99% confidence limit of identification. It is evident that the characterization procedure for valence-band spectra reported here is sensitive enough to describe the fine structure of the spectra to such an extent that every compound can be distinguished from any other compound, although the visual differences in spectral structure, are slight.

Those groups of spectra which show clear visual differences, such as those obtained from compounds giving narrow Fe $L_{\alpha 1,2}$ peaks (pure Fe, pyrite and marcasite) and broad peaks (the other compounds), show a large distance between their representation points. This gives an impression of the magnification of spectral differences obtained by mathematical processing of the spectra.

The sensitivity of distinction between different spectra is also evident from the fact that similar compounds, which show only a small difference in stoichiometry (such as FeS and $FeS_{1.1}$) can be clearly distinguished. It would be difficult to differentiate between FeS and $FeS_{1.1}$ by quantitative elemental analysis of Fe and S with an electron microprobe, because of the small difference in composition (63.53% Fe in FeS and 61.30% Fe in $FeS_{1.1}$).

A further advantage of the evaluation of the X-ray valence-band spectrum is that not only can information about the identity of the compound present be obtained, but also structural information, because the valence-band structure is influenced by the geometrical arrangement of the atoms. This can be seen from the different representation of cubic FeS_2 (pyrite) and rhombohedral FeS_2 (marcasite). Compounds with different structures can be clearly differentiated.

This is evidence that the measurement and evaluation of X-ray valence-band spectra (as described here) opens up the possibility of identifying very small changes in spectral structure at a high confidence level. This provides the basis for studying many minor

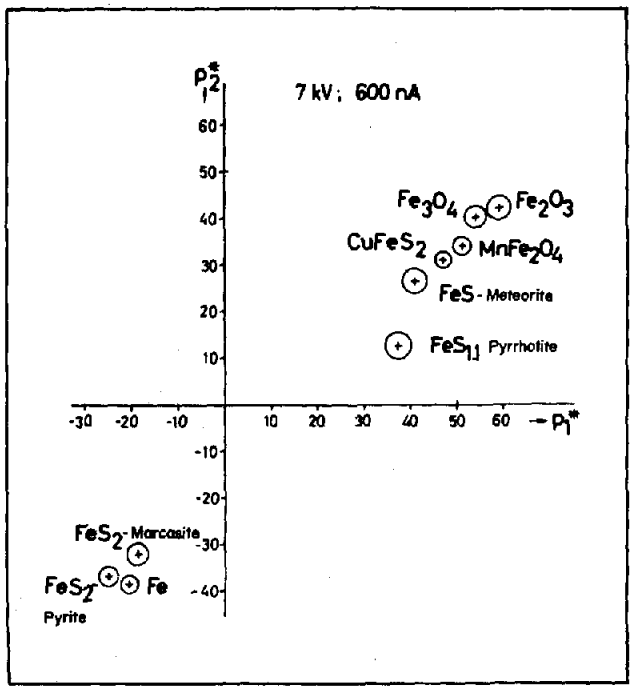

Fig. 3. Characterization of iron compounds in representative space. Diameter of circles corresponds to a confidence level of 0.99.

influences on the spectra, and from an analytical viewpoint, of evaluating these very small spectral features to obtain information, inaccessible by other means, concerning important properties of sample materials.

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KINETISCH-KATALYTISCHE BESTIMMUNGEN IN EINEM ZWEIPHASENSYSTEM UNTER VERWENDUNG EINES FALLROHRES

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Zusammenfassung—Eine einfache Methode zur Durchführung kinetisch-katalytischer Bestimmungen wird beschrieben, bei welcher die Reaktionspartner in zwei flüssigen miteinander nicht mischbaren Phasen gelöst sind. Tropfen der spezifisch schwereren Phase fallen durch die leichtere, welche in einem vertikalen Glasrohr ("Fallrohr") enthalten ist. Während des Fallens kommen die Reaktanten miteinander an der Phasengrenzfläche in Kontakt, was zu einer Veränderung des Tropfens führt. Die Fallhöhe bis zur Vollendung der Reaktion ist ein Maß für die Katalysatorkonzentration (z.B. Entfärbung des Tropfens in der Bestimmung von Kupfer mit Hilfe der Eisen(III)–Thiosulfatreaktion). Wenn als Reaktionsprodukt ein Gas (N_2, O_2) entsteht, welches am fallenden Tropfen sorbiert bleibt, dann steigt der Tropfen wieder auf. Sowohl Falltiefe als auch die Zeit, die der Tropfen benötigt, bis er wieder am oberen Ende des Fallrohres ankommt, stellen ein Maß für die Katalysatorkonzentration dar (z.B. Bestimmung von Thiosulfat mit der Jod–Azidreaktion und von Kupfer als Katalysator der Zersetzung von Wasserstoffperoxid).

Bei der zu beschreibenden Methode werden die Reaktionspartner in zwei flüssigen miteinander nicht mischbaren Phasen angewendet. Die leichtere der beiden Phasen befindet sich in einem etwa 1-m langen vertikalen Glasrohr ("Fallrohr"). Die andere, schwerere Phase fällt tropfenweise von oben durch die leichtere ruhende Phase im Fallrohr nach unten. Während dieses Fallens kommen die Reaktanten an der Phasengrenzfläche miteinander in Kontakt und die entsprechende Reaktion läuft ab, was zu einer visuell erkennbaren Veränderung des Tropfens (z.B. Farbänderung) führt.

Hier soll die Anwendung dieser Technik für kinetisch-katalytische Analysenmethoden diskutiert werden. Die Reaktanten reagieren miteinander unter sonst gleichen Bedingungen je nach der Konzentration des zu bestimmenden Katalysators unterschiedlich schnell. Je mehr Katalysator im System vorhanden ist desto eher (d.h. also nach desto kürzerer Falltiefe!) wird eine bestimmte Menge eines Reaktanten verbraucht oder eine bestimmte Menge des Reaktionsprodukt gebildet ("fixed concentration method"); dies bedeutet, daß sich aus der Falltiefe die Konzentration des Katalysators bestimmen läßt. Der Katalysator, also die Probe, kann je nach dem Reaktionssystem in der leichteren, ruhenden oder in der schwereren fallenden Phase enthalten sein.

Drei Beispiele sollen im weiteren diese neue Methode illustrieren.

EXPERIMENTELLER TEIL

Abbildung 1 zeigt eine schematische Darstellung der verwendeten Apparatur: das Fallrohr (a) wird von unten mit der leichteren Lösung (P_1) gefüllt. Durch die geeignete Stellung der beiden Dreiweghähne (b und c) wird die jeweils leichtere Phase mit Hilfe einer Kolbenspritze (e) aus dem Vorratsbehälter (d) bis etwa 1 cm unter den oberen Rand des Fallrohres gedrückt.

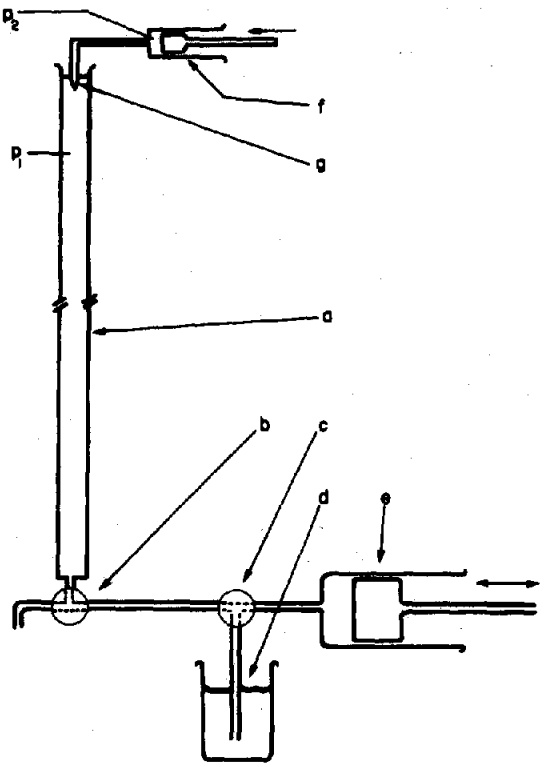

Abb. 1. Schematische Darstellung der Apparatur.

Die zweite schwerere Phase (P_2) wird tropfenweise, z.B. mit einer Kolbenbürette (f) (Infusionspumpe, Fa. Braun, Melsungen) durch die Kapillarspitze (g) direkt in die erste, leichtere Phase eingebracht. Durchmesser und Form dieser Spitze bedingen die Größe, die Geschwindigkeit der Kolbenbürette (z.B. 75 µl/min) die zeitliche Folge der Tropfen. Bei gleicher Tropfengröße ist die Fallgeschwindigkeit der Tropfen durch das Dichteverhältnis der beiden Phasen regelbar. Soll etwa ein Tropfen der schwereren organischen Phase durch eine leichtere wäßrige Phase fallen, so kann z.B. durch das Mischungsverhältnis von Chloroform und Petroläther die Dichte der organischen Phase variiert werden.

Läuft eine Reaktion verhältnismäßig langsam ab (geringe Katalysatorkonzentration), dann ist zur Erzielung einer ausreichend langen Reaktionszeit eine eher langsame Fallgeschwindigkeit und somit ein nur geringer Unterschied der Dichten der beiden Phasen wünschenswert. Die ablaufende Reaktion muß ja im (oder am) Tropfen eine erkennbare Veränderung liefern, ehe dieser das untere Ende des Fallrohres erreicht.

Bei den hier beschriebenen Beispielen wird diese Veränderung ausschließlich visuell beobachtet. Zwei Phänomene werden zur Indikation herangezogen.

Ein gasförmiges Reaktionsprodukt (Stickstoff, Sauerstoff) wird bevorzugt an der Tropfenoberfläche sorbiert und macht den Tropfen spezifisch leichter, so lange, bis er nicht mehr weiter fällt, sondern nach einem Stillstand wieder aufsteigt. Meßgröße ist die Falltiefe (Fallweg) des Tropfens oder die Zeit bis der Tropfen wieder am oberen Ende des Fallrohres angelangt ist.

Als zweites Phänomen dient die Entfärbung des fallenden Tropfens; Meßgröße ist hier die dazu benötigte Falltiefe.

Bestimmung von Thiosulfat

Thiosulfat katalysiert die Reaktion von Jod mit Azid zu Jodid und Stickstoff.[1,2]

Zur Bereitung der leichteren wäßrigen Phase werden jeweils 10 ml einer Natriumazidlösung (10 g NaN_3 + 15 g NaJ + H_2O ad 1000 ml) mit 5 ml der zu bestimmenden Thiosulfatlösung versetzt; davon werden 12 ml in das Fallrohr (95 cm lang, ~4 mm innerer Durchmesser) gegeben wie weiter oben beschrieben. Der Flüssigkeitsspiegel steht etwa 1 cm unter dem oberen Rand, die Kapillare taucht 1 cm tief in die wäßrige Lösung ein.

Eine gesättigte Lösung von Jod in Chloroform ist die schwerere Phase; sie wird durch die Kapillare tropfenweise eingegeben. Etwa alle 1,5 sec fällt ein Tropfen (*ca.* 3 µl; 75 µl/min Pumpgeschwindigkeit). Nach je 2 Tropfen wird die Bürette gestoppt und das Fallen der Tropfen beobachtet; dies wird 5–10 mal wiederholt.

Während ein Tropfen der Jodlösung durch die wäßrige Phase fällt, welche Azid und den Katalysator enthält, läuft die Reaktion ab; der dabei entstehende Stickstoff wird bevorzugt am Tropfen sorbiert, der Tropfen ($CHCl_3$ + N_2) wird insgesamt fortschreitend spezifisch leichter so lange bis er die Dichte der ihn umgebenden wäßrigen Phase unterschreitet und wieder aufsteigt.

Je höher die Konzentration des Katalysators Thiosulfat ist, desto schneller verläuft die Reaktion, desto weniger tief fällt der Tropfen, desto schneller kommt er oben (bei der Kapillarspitze) wieder an. Daher sind sowohl *Falltiefe* (in cm), als auch *Rückkehrzeit* (in sec) ein Maß für die Katalysatorkonzentration.

Abbildung 2 zeigt die mit Thiosulfat-Standardlösungen erhaltenen Eichkurven (47–470 µg $S_2O_3^{2-}$/12 ml). Die Meßwerte sind jeweils Mittelwerte aus der etwa zehnfachen Wiederholung der Beobachtung von je 2 Tropfen. Tabelle 1 zeigt die Resultate der Bestimmung von Thiosulfatproben.

Thioharnstoff, welcher gleichfalls die Jod-Azidreaktion katalysiert, wurde bei gleicher Arbeitsweise (12–120 µg/12 ml) bestimmt.

Bestimmung von Kupfer als Katalysator des Zerfalls von Wasserstoffperoxid

Kupfer als Tetramminkomplex katalysiert den Zerfall von Wasserstoffperoxid, wobei Sauerstoff gebildet wird.[3,4] Auch in diesem System wird wieder das Aufsteigen des Tropfens durch das gasförmige Reaktionsprodukt bewirkt.

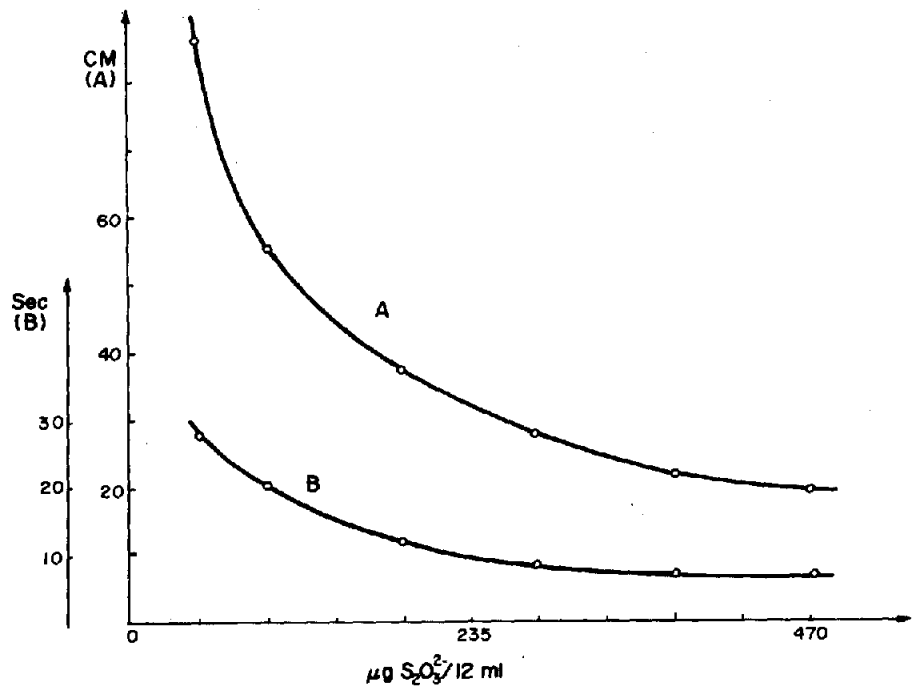

Abb. 2. Eichkurven zur Bestimmung von Thiosulfat; A = Auswertung der Falltiefe; B = Auswertung der Rückkehrzeit.

Tabelle 1. Bestimmung von Thiosulfat (alle Werte in μg $S_2O_3^{-2}$/12 ml)

gegeben	48	61	90	99	179	198	273	368	396	472
gefunden aus der Falltiefe	48	61	87	99	188	221	283	354	401	458
gefunden aus der Rückkehrzeit	49	60	90	96	175	215	295	360	388	430

Tabelle 2. Bestimmung von Kupfer (alle Werts in μg Cu^{2+}/10 ml ursprünglicher wässriger Probelösung)

gegeben	10	18	24	32	40	50	59	70	82	98
gefunden aus der Falltiefe	10	24	25	31	35	50	60	67	80	100
gefunden aus der Rückkehrzeit	10	20	28	33	40	48	60	70	85	110

In diesem Beispiel aber befindet sich der zu bestimmende Katalysator selbst in der schwereren Phase: 10 ml der wäßrigen Kupferlösung werden mit 2 ml einer Dithizonlösung (50 mg Dithizon in einer Mischung aus 200 ml Chloroform mit 40 ml Dichloräthan) extrahiert. Der so erhaltene Extrakt wird mittels der Kolbenbürette durch die wäßrige leichtere Phase (H_2O_2 30% + 2*M* Ammoniak 3:1) tropfen gelassen (Tropfenvolumen *ca.* 2,2 μl).

Der bei der Reaktion gebildete Sauerstoff wird am Tropfen sorbiert und bewirkt Stillstand und Wiederaufsteigen des Tropfens. Ausgewertet werden wiederum Falltiefe und Rückkehrzeit. Die Eichkurven sehen sehr ähnlich aus wie die im vorhergehenden Beispiel.

Die Standardlösungen enthalten 10 bis 100 μg Kupfer in 10 ml ursprünglich wäßriger Lösung; dies bedeutet, daß in den einzelnen Tropfen jeweils nur etwa 10–100 ng Cu enthalten sind.

Tabelle 2 gibt einige Ergebnisse solcher Bestimmungen.

Bestimmung von Kupfer als Katalysator der Reduktion von Eisen(III) durch Thiosulfat[5]

In diesem Beispiel wird die Entfärbung des fallenden Tropfens visuell beobachtet. Kupfer katalysiert die Reduktion von Eisen(III) durch Thiosulfat; der Ablauf der Reaktion wird durch das Verschwinden der Rotfärbung von Eisen(III)thiocyanat (in der schwereren organischen Phase) erkannt; der zu bestimmende Katalysator (Cu) befindet sich gemeinsam mit Thiosulfat in der leichteren wäßrigen Phase.

Zur Bereitung der organischen Phase werden 1 g Kaliumthiocyanat und 1 g Eisen(III)chlorid ($FeCl_3 \cdot 2H_2O$) in 50 ml dest. Wasser gelöst: Eisen(III)thiocyanat wird mit 25 ml Äther extrahiert. Die ätherische Lösung wird mit 50 ml Wasser einmal gewaschen und dann mit 50 ml Chloroform und 40 ml Aceton versetzt.

Die Zusammensetzung der organischen Phase hat folgende Gründe: Eisen(III)thiocyanat läßt sich besonders gut mit Äther extrahieren. Um die nötige Dichte zu erhalten, mußte Chloroform zu dieser Lösung zugesetzt werden. Dann ergab sich allerdings, daß der Übergang des Eisens in die wäßrige Phase nicht ausreichte. Durch Hinzufügen von Aceton konnte der zur Reaktion nötige Kontakt erreicht werden.

Die organische Phase wird in die Glasspritze (Infusionspumpe) gefüllt, sie ist nur wenig spezifisch dichter als die wäßrige Phase, daher fallen die Tropfen sehr langsam (72 cm/min).

Die wäßrige Phase ist eine Mischung von 30 ml einer 0,1*M* Thiosulfatlösung mit 10 ml der Kupfer-Probelösung; 25 ml dieser Mischung werden in das Glasrohr (110 cm lang, *ca.* 5,5 mm innerer Durchmesser) gefüllt.

Die Eisenlösung im organischen Medium wird mit 50 μl/min in die wäßrige Phase gepumpt. Alle 5 sec fällt ein Tropfen (*ca.* 4 μl) ab. Nach jeweils 4–6 Tropfen wird die Pumpe wieder gestoppt, um die Entfärbung der fallenden Tropfen zu beobachten.

Die Entfärbung der Tropfen wird gegen eine beleuchtete weiße Fläche beobachtet.

Die Fallstrecke entspricht einer Fallzeit (Reaktionszeit). Gemessen wird die Strecke bis der Tropfen eine immer gleiche schwache Gelbfärbung erreicht hat. Dieser Farbton ist besser zu erkennen als die vollständige Entfärbung.

Die in Abb. 3 gezeigte Eichkurve wurde mit Kupferlösungen erhalten, die in dem Volumen, das zur Messung verwendet wird, 62,5–625 μg Cu gelöst enthalten. Tabelle 3 zeigt einige Ergebnisse von Kupferbestimmungen.

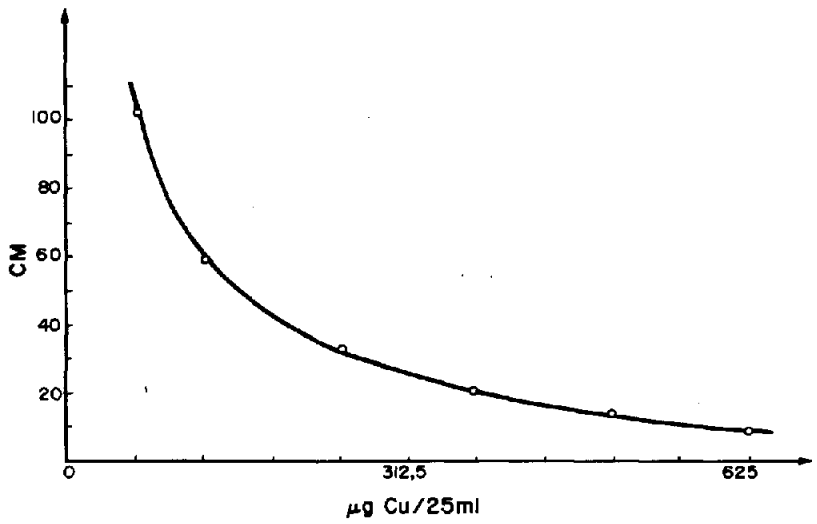

Abb. 3. Eichkurve zur Bestimmung von Kupfer (Entfärbung).

Tabelle 3. Bestimmung von Kupfer (alle Werte in μg Cu^{2+}/25 ml)

gegeben	63	87	144	238	266	338	406	463	544	609
gefunden	66	88	163	222	281	344	438	525	500	613

DISKUSSION

Wie die Ergebnisse (vgl. Tab. 1–3) zeigen, erlaubt die von uns als "Fallrohrtechnik" bezeichnete Methode die bequeme Durchführung von kinetisch-katalytischen Bestimmungen mit zufriedenstellender Genauigkeit. Wenn der zu bestimmende Katalysator in der leichteren (in den angeführten Beispielen also in der wäßrigen) Phase vorliegt, ist natürlich die Empfindlichkeit viel geringer als in jenen Fällen, bei denen der fallende Tropfen selbst den Katalysator enthält.

Die an sich wohl schon recht einfache Versuchsanordnung kann noch weiter vereinfacht werden; so kann etwa die Tropfenzugabe auch mit Hilfe einer manuell bedienten Kolbenbürette erfolgen.

Als Fallrohr kann ein einfaches Glasrohr ohne jede Vorrichtung zum Füllen dienen, doch ist die in Abb. 1 (b–d) dargestellte Anordnung bequemer und ermöglicht vor allem einen raschen Wechsel der leichteren Phase. Es sei darauf hingewiesen, daß die Erneuerung der Phase im Glasrohr (die ja oft den zu bestimmenden Katalysator enthält) wohl leicht auch kontinuierlich (im Durchfluß) ausführbar ist.

Zum Schluß sei noch erwähnt, daß in unserem Arbeitskreis einige katalytisch-kinetische Bestimmungen in einem Reaktionssystem mit zwei ruhenden flüssigen übereinandergeschichteten nicht mischbaren Phasen ausgeführt wurden. Die Verfolgung des Reaktionsablaufs geschah thermometrisch; in jede der beiden Phasen tauchte dabei ein Thermistor. Das Maximum der auftretenden Temperaturdifferenz stellt ein Maß dür die Konzentration des zu bestimmenden Katalysators dar.[6]

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Summary—A rather simple method for kinetic-catalytic determinations is described, in which the reactants are dissolved in two immiscible liquid phases. Drops of the heavier phase fall through the lighter one contained in a vertical glass tube. As the drops fall, the reactants come into contact with each other at the interface, thus causing a change in the drops. The length of fall needed for completion of reaction is a measure of the concentration of the catalyst (*e.g.*, decolorization of the drops in the determination of copper by the reaction between iron(III) and thiosulphate). If a gaseous reaction product is formed (*e.g.*, N_2 or O_2) and adsorbed on the falling drop, then the drop stops falling and rises again. The depth of fall or the time needed for the drop to return to the upper end of the tube can be used as a measure for the concentration of catalyst (*e.g.*, determination of thiosulphate with the iodine/azide reaction, or of copper as catalyst for the decomposition of hydrogen peroxide).

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SÄULEN ZUR BESTIMMUNG KLEINER PROBEMENGEN (10^{-10} g) IN DER FLÜSSIGKEITS-CHROMATOGRAPHIE

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Zusammenfassung—Die Verdünnung der Probe in der flüssigkeitschromatographischen Säule nimmt quadratisch mit dem Innendurchmesser der Säule zu, falls alle anderen Parameter konstant gehalten werden. Sind die Probemengen (-volumina) sehr klein, können die getrennten Komponenten nicht mehr nachgewiesen werden. Für geringe Probemengen wären die irregulär gepackten Kapillarkolonnen mit einem Innendurchmesser weit unter 1 mm die ideale Lösung. Da die Masse der stationären Phase pro Volumeneinheit in diesen Säulen sehr gering ist (kleine k'-Werte und große Totzeiten), werden die Analysenzeiten und die Verdünnung der Probe im Eluenten groß und es treten wesentliche apparative Schwierigkeiten auf. Apparatur und Methode für die Packung von Glassäulen mit einem Innendurchmesser von 1,3 mm bis 2 mm werden beschrieben. Die Säulen werden mit Silikagel und mit Umkehrphasen (d_p = 10 μm) gepackt und es werden h/d_p-Werte zwischen 2,5 und 4 erzielt. Wie bei den Säulen mit größerem Innendurchmesser sind die h-Werte für die beiden stationären Phasen sehr ähnlich (Eluent: n-Heptan und Methanol). Es wird gezeigt, daß die *cis*- und *trans*-Isomeren der Abscisinsäure getrennt werden können bei einer Probemenge von 10^{-10} g, allerdings sind die molaren Extinktionskoeffizienten groß.

Bei der "Spurenanalyse" in der Flüssigkeits-Chromatographie sind zwei grundsätzlich verschiedene Probleme zu unterscheiden.

I. Die Konzentration einer oder einiger Komponenten in der Probe ist gering, es stehen jedoch praktisch unbegrenzte Probemengen zur Verfügung. In diesem Fall kann man mit beliebigem Säulendurchmesser arbeiten solange die Belastbarkeit der Säule (d.h. Probemasse pro Gramm stationäre Phase) konstant gehalten wird. Typisches Beispiel für diesen Fall ist die Bestimmung von organischen Verunreinigungen in Wasser, wobei das Problem der Aufkonzentrierung hier nicht diskutiert werden soll.

II. Die zur Verfügung stehende Probemenge ist außergewöhnlich klein. Derartige Probleme treten in der Biologie oder der Medizin des öfteren auf. Hier sind kleine Säulendurchmesser gefordert, um die unerwünschte Verdünnung der Probe im Eluenten (Detektionsprobleme) zu vermeiden.[1]

Bisher galt es als Erfahrungstatsache, daß die Effizienz der gepackten Säulen mit einem Innendurchmesser von weniger als 3 mm mit abnehmendem Innendurchmesser außergewöhnlich stark sinkt.[2,3] In dieser Arbeit soll eine Packungsmethode beschrieben werden, die die Herstellung von Säulem mit i.D. von 1,3 mm bis 2,1 mm—ohne Verlust an Effizienz und Permeabilität—zuläßt.

SYMBOLVERZEICHNIS

A^*	Konstante in Gl. (4)
C^*	Konstante in Gl. (4)
d_c	Innendurchmesser der Säule
D_m	Diffusionskoeffizient der Probe im Eluenten
d_p	Teilchendurchmesser
F	Volumenflußgeschwindigkeit
h	Höhenäquivalent eines theoretischen Bodens
h^+	h-Wert für u = 1 mm/sec berechnet
K	Permeabilität
k'	Kapazitätsverhältnis
K_F	Permeabilität auf die Leerrohrgeschwindigkeit bezogen
L	Säulenlänge
N	Zahl der effektiven Böden
n	Zahl der theoretischen Böden
r	Säulenradius
s	Probemasse
u	lineare Geschwindigkeit
α	relative Retention
Δp	Druckabfall
ϵ_T	totale Porosität
ϵ_λ	molarer Extinktionskoeffizient
η	Viskosität
ω	Standardabweichung des Peaks in Volumeneinheiten

Diese Säulen sollen mit Probenvolumina von 1 bis 10 μl beschickt werden können, da diese Volumina experimentell bequem handhabbar sind. Weiterhin sollte die chromatographische Apparatur weitgehend aus handelsüblichen Bauelementen zusammengestellt werden.

In der Flüssigkeits-Chromatographie kann erfahrungsgemäß[4] eine Säule dann als gut gepackt betrachtet werden, wenn ihre Effizienz mit der Gleichung:

$$h = 3d_p + \frac{6}{u} + \frac{d_p^2 u}{20} \qquad (1)$$

beschrieben werden kann. In Gleichung (1) wird die relative Bandenverbreiterung h (oder Höhenäquivalent eines theoretischen Bodens) und die Teilchengröße d_p in μm und die lineare Geschwindigkeit

des Eluenten u mm/sec Einheiten angegeben. Es wird ein Diffusionskoeffizient von etwa $3 \cdot 10^{-5}$ cm²/sec (d.h. der Eluent ist Heptan oder Methylenchlorid) und ein Kapazitätsverhältnis k' zwischen 0 und 2 vorausgesetzt. Die Gleichung (1) ist nur gültig, falls d_p an Hand chromatographischer Messungen mit

$$d_p = 10^3 K_F = \frac{10^3 F \eta L}{r^2 \pi \Delta p} \qquad (2)$$

definiert ist.

Analytische Anwendungen von Säulen mit i.D. < 3 mm wurden schon beschrieben. Horwitz *et al.*[5] berichten über "mini columns" mit 2–3 mm i.D. und 2–4 cm Länge [$d_p \simeq 5$ μm]. Um das kleine Kolonnenvolumen zu kompensieren, sind die Kapazitätsverhältnisse außergewöhnlich hoch ($k' = 10$–30). Außerdem wird ein sehr empfindlicher radiochemischer Detektor verwendet.

Ishii *et al.*[6] packen 8–50 cm lange Teflonschläuche von 0,25–0,5 mm i.D. mit Silikagel ($d_p \simeq 10$ μm). Allerdings muß ein ungewöhnliches Probenaufgabesystem mit "stop flow" Technik und ein UV-Detektor mit einem Zellenvolumen von *ca.* 0,4 μl eingesetzt werden. Die Effizienz dieser Säulen ist gut solange die Probenvolumina kleiner sind als 0,01 μl.[7] Nach Zitaten 1 und 8 läßt sich jedoch berechnen, daß bei Säulen mit den angegebenen Dimensionen und Effizienzen erst Probevolumena, die über 20mal größber sind, eine merkliche (über 10%) zusätzliche Bandenverbreiterung hervorrufen sollten.

Verwendbarkeit der irregulär gepackten Kapillarkolonnen in der Flüssigkeits-Chromatographie

Ist die zur Verfügung stehende Probemenge sehr klein, so scheinen die gepackten Kapillarkolonnen[9,10] mit einem i.D. weit unter 1 mm die ideale Lösung zu sein. Diese irregulär gepackten Säulen sind dadurch gekennzeichnet, daß das Verhältnis Innendurchmesser/Teilchengröße (d_c/d_p) kleiner als 5 ist (vorzugsweise 2–4). In der Gaschromatographie war die Effizienz h dieser Säulen vergleichbar mit den entsprechenden Werten, die mit gepackten Säulen erzielt wurden, falls die Teilchengrößen identisch waren. Allerdings war die Permeabilität K der irregulär gepackten Säulen mit einem Faktor von *ca.* 10 besser als die der regulär gepackten. Demzufolge konnte man längere irregulär gepackte Säulen mit identischem Druckabfall verwenden. Bedingt durch die kleinere Masse an stationärer Phase pro Volumeneinheit der Säule war es nachteilig, daß bei den irregulär gepackten Säulen

(*a*) die zulässigen Probemassen sehr gering waren, deshalb mußte die injizierte Probe gesplittet werden, und

(*b*) nur Systeme mit großen Bunsen'schen Verteilungskoeffizienten zulässig waren, um die Kapazitätsverhältnisse k' der Proben groß zu halten.

In der Flüssigkeits-Chromatographie wurden Kupfersäulen ($d_c = 2$ mm) mit Glasperlen ($d_p = 0{,}5$ mm) nach der klassischen gaschromatographischen Methode gepackt ($d_c/d_p = 4$).[11] Für den Inertpeak konnte bei hohen Geschwindigkeiten zwischen 10 und 30 cm/sec $h = 2$ mm erzielt werden, was einem $h/d_p = 4$ Verhältnis entsprach.

Arbeitete man mit irregulär gepackten Kapillarkolonnen aus Glas, die nach den beschriebenen Methoden[9,10] gezogen wurden, so waren die Säulen nicht gut reproduzierbar, die h-Werte nahmen mit zunehmender Retention steil zu und sämtliche Probleme dieses Säulentyps in der Flüssigkeits-Chromatographie wurden sichtbar.[12]

Diese Probleme sollen an Hand der Meßergebnisse von Tsuda und Novotny[13] diskutiert werden. Sämtliche Daten wurden aus der einzigen Trennung in dieser Arbeit (Abb. 8) entnommen. Die Kolonne ist 29 m lang ($d_c = 75$ μm) und mit Aluminiumoxid ($d_p = 30$ μm) gepackt ($d_c/d_p = 2{,}5$). Die mobile Phase ist n-Hexan mit 0,05% Methanol ($\eta = 0{,}3$ cP). Die lineare Geschwindigkeit des Eluenten ist mit $u = 0{,}65$ cm/sec angegeben. Um die nicht angegebene Volumengeschwindigkeit F zu errechnen, muß die totale Porosität ϵ_T angenommen werden. Erfahrungsgemäß ist bei klassisch gepackten Säulen $\epsilon_T > 0{,}8$. Wegen der loseren Packung und besseren Permeabilität soll hier $\epsilon_T = 0{,}9$ angenommen werden. Dies steht mit eigenen Messungen im Bereich der Gaschromatographie bzw. Flüssigkeits-Chromatographie in Einklang. Dementsprechend berechnet sich die Flußgeschwindigkeit zu $F = 1{,}55$ μl/min. Die Permeabilität wird mit $6{,}1 \cdot 10^{-8}$ cm² angegeben und ist somit *ca.* 7 mal besser als die entsprechender regulär gepackter Säulen. Der Druckabfall an der Säule beträgt 102 atm. Wegen der geringen Flußgeschwindigkeit bei hohem Druck wird zwischen Probenaufgabe und Säuleneingang 1:1000 gesplittet. Der Vergleich mit der angegebenen Eluentengeschwindigkeit zeigt, daß Benzol in etwa inert durchbricht ($k' \simeq 0$). Für Chinolin—die Probe mit der längsten Retentionszeit in der Trennung—ist das Kapazitätsverhältnis sehr klein ($k' = 0{,}24$). Arbeitete man mit "trockenem" Heptan als Eluent, so würden die Retentionen wachsen, allerdings ist die Konstanthaltung des geringen Wassergehaltes schwierig und die Peaks werden asymmetrischer. Für Chinolin werden 85,000 theoretische Böden ($h = 341$ μm) innerhalb 100 Minuten erzielt. Der h-Wert stimmt mit dem, nach Gleichung (1) für gepackte Säulen errechneten, gut überein. Wegen des kleinen k'-Wertes entspricht dies aber nur 3184 effektiven Böden N und dadurch kann man nur bei einer relativen Retention $\alpha = 1{,}12$ Basislinientrennung erzielen. Derartige Trennungen sind mit gepackten Säulen ohne Schwierigkeiten innerhalb wesentlich kürzerer Zeiten zu erreichen. Mit dieser gepackten Kapillarsäule werden nur 0,53 effektive Böden pro Sekunde erzielt.

Charakterisiert man das Peakvolumen des Chinolins mit der vierfachen Standardabweichung des Peaks, so errechnet man aus den h, L und d_c Werten *ca.* 1,5 μl. Da das Zellenvolumen des verwendeten Detektors aber 8 μl beträgt, wird der Strom zwischen

Säulenausgang und Detektoreingang mit zusätzlichen Eluenten verdünnt ("make up flow"). Diese Zusatzflußgeschwindigkeit wird mit 20–50 µl/min angegeben. Setzt man die geringste Verdünnung (20/1,55 = 13) voraus, so beträgt das verdünnte Peakvolumen *ca.* 20 µl und die Detektionsprobleme sind gelöst. Die Probemenge wird mit *ca.* 10^{-8} g angegeben. Dies entspricht am Peakmaximum in etwa 1 ppm Chinolin in Hexan. Wesentlich größere Verdünnung wäre auch nicht gestattet, da das Detektorsignal bei dem obigen Peakmaximum unweit vom Rauschpegel des Detektors liegt.

Zusammenfassend. Die *h*-Werte in irregulär gepackten Kapillarkolonnen in der Flüssigkeits-Chromatographie sind vergleichbar mit denen, die in klassisch gepackten Säulen erzielt werden, falls beide Säulen mit einer identischen Charge der stationären Phase gepackt wurden. Die Permeabilitäten sind in den irregulär gepackten Säulen 5–10 mal größer, Demzufolge kann man hier längere Säulen mit gleichem Druckabfall (u = const.) verwenden. Bedingt durch die geringere Masse an stationärer Phase sind die folgenden Nachteile in Kauf zu nehmen: (1) Probemengen in der Größenordnung von 10^{-8} g zwingen zum Splitten vor der Säule, (2) die Kapazitätsverhältnisse der Proben sind klein; demzufolge werden zwar hohe theoretische Bodenzahlen produziert, das Auflösungsvermögen ist aber, an den n Werten gemessen, bescheiden, (3) wegen der kleinen Peakvolumina muß nach der Säule verdünnt werden ("make up flow") und dadurch sinkt die Nachweisgrenze der einzelnen Komponenten, (4) die Analysengeschwindigkeiten sind wesentlich kleiner als mit klassisch gepackten Säulen, (5) der Aufbau der Apparatur ist, wegen der beiden Splitt-Systeme, aufwendig.

Klassisch gepackte Säulen mit geringem Innendurchmesser

Stehen nur sehr kleine Probemengen zur Verfügung ($s < 10^{-7}$ g), so ist eines der zentralen Probleme in der Flüssigkeits-Chromatographie die unvermeidliche Verdünnung dieser Probemenge im Eluenten möglichst niedrig zu halten, um die Nachweisgrenze im Detektor zu gewährleisten. Selbstverständlich muß die Probe wenn möglich in großer Konzentration bei der Probenaufgabe vorhanden sein. Das Peakvolumen am Ende der Säule 4ω soll klein werden, wobei

$$\omega = r^2\pi\epsilon_T\sqrt{hL} = r^2\pi L\epsilon_T\sqrt{\frac{1}{n}} \qquad (3)$$

(r der Radius der Kolonne und ϵ_T die totale Porosität ist). Für Kieselgel liegt letztere bei klassisch gepackten Säulen um 0,84, bei irregulär gepackten Säulen zwischen 0,9 und 0,95. Die Verdünnung nimmt also quadratisch mit dem Säulenradius und linear mit der Länge der Säule zu, ist aber umgekehrt proportional mit $\sqrt{n}$. Will man die Verdünnung klein halten, so muß das Säulenvolumen, insbesondere aber der Durchmesser der Säule, klein und die Bodenzahl n groß gehalten werden.

Die Bandenverbreiterung außerhalb der Säule (Probenaufgabe, Verbindungsröhre, Detektorvolumen, usw.) kann zwar klein gehalten werden, aber mit abnehmendem Kolonnenvolumen nimmt die Bandenverbreiterung, die durch diesen Effekt verursacht wurde, relative immer zu. [Sind die Bandenverbreiterungseffekte außerhalb der Säule nicht zu vernachlässigen, so nehmen erfahrungsgemäß die *h*-Werte mit zunehmender Retentionszeit (*k'*-Werte) ab.] Zwangsläufig treten also apparative Schwierigkeiten auf, wenn das Volumen der Säule sehr stark abnimmt. Erfahrungsgemäß sind diese Probleme zu beherrschen solange der Innendurchmesser der Säule größer als 1 mm und die Länge über 10 cm ist.

Die Verdünnungseffekte wurden im vorherigen Kapitel an numerischen Beispielen demonstriert. Sie können in tragbarer Näherung auch quantitativ abgeschätzt werden.[1,14]

An Hand dieser Überlegungen soll eine Packungsmethode für Säulen mit einem Innendurchmesser zwischen 1 und 3 mm beschrieben werden, wobei die Effizienz dieser Säulen vergleichbar sein soll mit denen, die einen Innendurchmesser von 3–10 mm haben und deren Effizienz mit den Gleichungen (1) und (2) gut angenähert wurde.

EXPERIMENTELLER TEIL

Packung der Säulen

Säulenmaterial. Zahlreiche Versuche in unserem[2,15] und anderen Labarotorien[3,16] haben gezeigt, daß Stahlröhren mit einem Innendurchmesser unter 3 mm wesentlich uneffizienter sind als die mit einem Innendurchmesser zwischen 3 und 8 mm. Um Glasröhren mit hohen Eingangsdrücken packen zu können, wurde eine Trennsäule der Firma Riedel–de Haen, Seelze-Hannover, verwendet. Diese Glassäule ist mit einem Druckmantel aus Stahl umgeben, so daß der Druck von außen nach innen wirkt. Die Innendurchmesser derartiger Säulen waren 1,3, 1,5, 1,9, 2,0 und 2,1 mm, die Säulenlänge betrug 30 bzw. 30,5 cm.

Stationäre Phasen. Die Säulen wurden sowohl mit Kieselgel als auch mit Umkehrphasen gepackt. Das verwendete, kommerziell erwerbliche Kieselgel (LiChrosorb Si 100, Fa. Merck AG, Darmstadt) hatte eine Teilchengröße von 10 µm. Die C_{18}-Umkehrphase wurde auf diesem Silikagel nach der Methode von Schmidt[17] hergestellt. Der Kohlenstoffgehalt dieser Umkehrphase betrug 17,2 Gew. %.

Packungssuspensionen. Die Kieselgelsäulen wurden nach dem "balance-density-slurry"-Verfahren[18,19] gepackt. Die Suspension setzte sich aus 40 Vol. % 1,1,2,2-Tetrabromäthan, 30 Vol. % Tetrachlorkohlenstoff und 30 Vol. % Dioxan zusammen. Die Umkehrphasen wurden nach der Viskositätsmethode[19] gepackt. Die Zusammensetzung der Packungssuspension war 40 Vol. % Cyclohexanol in Propan-2-ol.

Das Volumen am Suspensionsmittel wurde so gewählt, daß die Konzentration der festen stationären Phase etwa 40 mg/ml Suspension betrug. Die Menge der Suspension wurde so gewählt, daß am Ende der Packungsprozedur ein geringer Teil des Packungstopfes auch noch mit stationärer Phase gefüllt war. Dadurch wurde eine homogene Packung innerhalb der Säule bis zu ihrem oberen Ende erzielt.

Packungsapparatur und Methode. Wurde die Säule mit Kieselgel gepackt, so wurde eine Pumpe verwendet, deren maximaler Ausgangsdruck 600 atm betrug (Typ AE 10 der Fa. Orlita, Gießen). Für die Viskositätsmethode mußte eine Pumpe mit einem maximalen Ausgangsdruck von 1500 atm (Typ MK 1 S 80 der Firma Orlita), verwendet werden.

Die Anfangsflußgeschwindigkeit betrug bei 2 mm Innendurchmesser etwa 2,5 ml/min und bei 1,3 mm Innendurchmesser *ca.* 1,5 ml/min. Das Hubvolumen der Pumpe wurde am Anfang so eingestellt, daß die obigen Werte erzielt wurden. Während des Packungsvorganges nimmt der pneumatische Widerstand der Säule konstant zu. Da Kolbenmembranpumpen verwendet wurden, sank—entsprechend der Fördercharakteristik—die Flußgeschwindigkeit. Deswegen sank die Flußgeschwindigkeit nach 1 min auf die Hälfte bis 1/3 des Anfangsflusses. Man erhöhte das Hubvolumen der Pumpe kontinuierlich so, daß die Flußgeschwindigkeit bis zum Ende des Packungsvorganges bei den Werten, die nach 1 min erreicht waren, konstant blieb. Bis zum Ende des Packungsvorganges stieg der Druck bei der Viskositätsmethode auf max. 1100 atm.

Die Packungssuspension wurde mit n-Heptan überschichtet und der Durchbruch des Heptans (Ende des Packungsvorganges) wurde durch den wesentlichen Abfall des Eingangsdruckes angezeigt. Nach Beendigung des Packungsvorganges wurden die Säulen etwa 10 min bei hohen Flußgeschwindigkeiten (10–20 mm/sec) mit n-Heptan gespült.

Wie aus den oben angegebenen Daten ersichtlich, soll man mit abnehmendem Innendurchmesser der Säule zunehmende Packungsgeschwindigkeiten verwenden, um gute Säulenpackungen zu erzielen.

Nach unseren Erfahrungen konnte man Glassäulen mit einem Innendurchmesser unter 2,1 mm und mit einem Außendurchmesser von 8–9 mm mit Eingangsdrücken bis zu 100 atm ohne Druckmantel belasten. Dementsprechend wurden die Glassäulen nach dem Packungsvorgang aus dem Stahlmantel ausgebaut. An beiden Enden wurden mit einem handelsüblichen Zweikomponenten-Epoxykleber Metallfittings angebracht. Die Entfernung des Druckmantels war notwendig, da dadurch optimale Effizienz in der Flüssigkeits-Chromatographie Apparatur erzielt wurde.

Apparatur

Pumpe. Zwei-Kopf Membranpumpe (Typ: DMP-AE 10.4 der Firma Orlita, Gießen). Zwischen Pumpe und Probenaufgabe wurde ein Pulsationsdämpfergerät der Firma Orlita eingebaut.

Probenaufgabe. Type 7120 der Firma Rheodyne, Berkeley, Calif., mit 20 μl Schleifenvolumen. Dieses kommerziell erwerbliche Probenaufgabesystem verursachte nicht tragbare Bandenverbreiterungen falls der Innendurchmesser der Säule kleiner war als 1,5 mm ($L = 30$ cm). In den letztgenannten Fällen wurde die Probe direckt auf das Säulenpackungsmaterial aufgegeben Septuminjektor.[20]

Detektor. Die Zellvolumina des im Eigenbau hergestellten UV-Detektors (254 ± 8 nm) betrugen 10 bzw. 1 μl. Die größere Meßzelle verursachte keine Verfälschung der Peakformen solange der Innendurchmesser der Säule nicht kleiner war als 2 mm.

Eluent. Der Eluent war n-Heptan und die Proben brachen an den Silikagelsäulen mit den folgenden Kapazitätsverhältnissen durch: Tetrachloräthylen TCÄ ($k' = 0$), Anthracen ($k' \cong 0{,}6$) und Chrysen ($k' \cong 1{,}1$).

In den mit Umkehrphasen gepackten Säulen war der Eluent Methanol und als Proben wurden die folgenden Substanzen eingesetzt: Nitromethan ($k' = 0$), Anthracen ($k' \cong 0{,}6$) und Chrysen ($k' \cong 1{,}25$).

Sämtliche Messungen wurden bei Zimmertemperatur durchgeführt. Die linearen Geschwindigkeiten des Eluenten lagen zwischen 1 und 6 mm/sec und der Druckabfall an der Säule war immer kleiner alß 100 bar.

MESSERGEBNISSE

Für alle Säulen, die in dieser Arbeit beschrieben werden, gilt, daß der Asymmetriefaktor A_s^2 kleiner als 1,1 war.[19] Eine weitere Grundvoraussetzung war die Beständigkeit gegen mehrmaligen Eluentenwechsel. Dabei mußten Effizienz und Permeabilität der Säule unverändert bleiben, wenn bei den mit Silikagel gepackten Säulen n-Heptan und Methylenchlorid und bei den mit Umkehrphase gepackten Säulen n-Heptan–Methylenchlorid–Methanol–Wasser des öfteren gewechselt wurden.

In dem untersuchten Geschwindigkeitsbereich ($u = 1$–6 mm/sec) konnte man die Meßergebnisse in sehr guter Näherung mit der folgenden Gleichung beschreiben:

$$h = A^* + C^* u \qquad (4)$$

Selbstverständlich sind die Konstanten A^* und C^* mit den korrespondierenden Konstanten der van Deemter-Gleichung nicht identisch. In Tabelle 1 sind diese Konstanten und die h-Werte bei einer Geschwindigkeit von 1 mm/sec (hier h^+) eingetragen. Die letztgenannten Werte können als typisch betrachtet werden, da es aus mehreren Gründen empfehlenswert ist, bei Säulen, die mit 10-μm Teilchen gepackt sind,

Tabelle 1. Konstanten der Gleichung: $h = A^* + C^* u$

		TCÄ ($k' = 0$)			Anthracen ($k' \approx 0{,}6$)			Chrysen ($k' \approx 1{,}25$)		
i.D., *mm*	d_p, μm	A^*, μm	C^*, *msec*	h^+, μm	A^*, μm	C^*, *msec*	h^+, μm	A^*, μm	C^*, *msec*	h^+, μm
2,1	10,1†	35,3	6,3	41,6	35,3	8,2	43,5	30,4	10,3	40,7
2,0	9,7‡	29,2	3,8	33,0	30,0	5,7	35,7	30,8	6,8	37,6
2,0	9,6‡	22,6	8,9	31,5	25,1	9,0	34,1	20,9	12,0	32,9
1,5	9,7‡	19,1	6,2	25,3	17,4	9,0	26,4	14,5	10,3	24,5
		Nitromethan ($k' = 0$)			Anthracen			Chrysen		
1,9	9,8§	26,6	5,8	32,4	21,7	11,3	33,0	22,2	12,9	35,1
1,3	9,5§	35,2	11,4	46,6	36,1	11,4	47,5	34,6	12,5	47,1

$h^+ = h$ bei $u = 1$ mm/sec.
‡ Stationäre Phase: Silikagel, Eluent: n-Heptan.
§ Stationäre Phase: C_{18} Umkehrphase, Eluent: Methanol.

bei dieser Geschwindigkeit zu arbeiten. Die Vorteile sind u.a.: der Druckabfall an der Säule wird relativ gering gehalten, die Säulenlänge kann kurz gewählt werden und die Effizienz ist kaum eine Funktion der Kapazitätsverhältnisse der Probesubstanzen. In der Tabelle 1 sind die h, A* und d_p-Werte in μm, die C^*-Werte in msec und u in mm/sec-Einheiten anzugeben, da diese Einheiten typisch und charakteristisch für derartige Säulen sind. Die in der Spalte 2 der Tabelle 1 angegebenen Teilchengrößen d_p wurden mit Hilfe von Gleichung (2) chromatographisch bestimmt. Es soll darauf hingewiesen werden, daß diese d_p-Werte nicht nur von der Güte der Siebfraktion der verwendeten stationären Phase abhängig sind, sondern sie beinhalten auch die Güte bzw. Reproduzierbarkeit der Packungsmethode. Nur ein Teil der Meßergebnisse ist in Tabelle 1 angegeben. Es wurden bewußt Säulen ausgewählt, mit deren Hilfe man die maximale Streuung der Meßergebnisse charakterisieren kann.

Sämtlichl in der Tabelle 1 angegebenen Kolonnen wurden mit derselben Silikagelcharge gepackt. Die geringe Streuung der chromatographisch bestimmten d_p-Werte (9,5–10,1 μm) weisen auf die Reproduzierbarkeit der Säulenpackung betreffend deren Permeabilität hin.

Betrachtet man die Streuung der A^* und C^*-Werte für eine Probesubstanz als Funktion des Innendurchmessers der Säule (z.B. die dritte und vierte Kolonne in Tabelle 1), so sind die Streuungen groß. Dies kann mit wenig Erfahrungen bei der Packung derartiger Säulen erklärt werden. Ähnliches gilt für die Streuung der h^+-Werte innerhalb einer Kolonne. Allerdings werden ähnliche Effizienzen erzielt, wie sie mit Gleichung (1) zu berechnen sind und die typisch sind für Säulen mit Innendurchmessern von 3 bis 8 mm. Die h^+-Werte (bei u = 1 mm/sec) entsprechen einem h/d_p Verhältnis von 2,5–4.

Überraschenderweise sind die A^*, C^* und h^+-Werte innerhalb einer Säule (also eine Zeile in Tabelle 1) in erster Näherung unabhängig von der Qualität bzw. dem Kapazitätsverhältnis der einzelnen Probesubstanzen. Vergleicht man die Konstanten von Säulen, die mit Silikagel bzw. mit Umkehrphase gepackt wurden, so sind die Werte ähnlich. Dies ist überraschend, da die Diffusionskoeffizienten der Probesubstanzen in n-Heptan bzw. Methanol sich voneinander unterscheiden.

Die Daten der Tabelle 1 zeigen, daß man Säulen mit einem Innendurchmesser von 1,3 bis 2,1 mm mit der in dieser Arbeit angegebenen Methode einigermaßen reproduzierbar packen kann und die Effizienz dieser Säulen vergleichbar ist mit der der in der Routine der Chromatographie eingesetzten Säulen mit einem Innendurchmesser von 4,2 mm.[21]

Um auf die apparativen Schwierigkeiten hinzuweisen, die auftreten, falls man mit Säulen geringerer Durchmesser arbeitet, sind in Tabelle 2 die Peakvolumina (4 ω) aufgelistet. Diese Werte wurden an Hand der experimentell bestimmten Effizienzen mit Hilfe der Gleichung (3) errechnet. Wie ersichtlich, werden auch Peakvolumina unter 16 μl bestimmt. Selbstverständlich kann man in diesen Fällen keine Detektoren mit einem Zellenvolumen von 10 μl einsetzen und man muß auch darauf achten, daß sowohl bei der Probenaufgabe als auch in den Verbindungsröhren nur sehr geringe Bandenverbreiterungen auftreten.

Die voneinander etwas abweichenden Kapazitätsverhältnisse in der Tabelle 2 wurden durch die minimalen Veränderungen des Wassergehaltes im Eluenten (n-Heptan) verursacht.

Bei den Messungen, die in Tabelle 1 eingetragen sind, betrug die Probemenge immer $6 \cdot 10^{-7}$ g und das Probevolumen war 1 μl. Dementsprechend war die Konzentration der Probe im Lösungsmittel *ca.* 600 ppm. Da die Peakvolumina in Tabelle 2 in μl-Einheiten angegeben sind, ergeben diese Zahlenwerte auch die Verdünnung der Probe bedingt durch die Wanderung innerhalb der Säule. Beträgt das Peakvolumen z.B. 65 μl, so ist die Konzentration der Probe am Ende der Säule < 10 ppm.

Effizienz als Funktion des Probevolumens

Je größer das Probevolumen, um so weniger wird die wünschenswerte Randbedingung erfüllt, daß die Probe "punktförmig" auf den Eingang der Säule aufgegeben wird. In Abbildung 1 werden die h-Werte—bei sonst unveränderten Bedingungen—als Funktion

Tabelle 2. Peakvolumina (4ω) in verschiedenen Säulen bei u = 1 mm/sec

System	L, cm	i.d., mm	u, mm/sec	TCÄ k'	TCÄ h, μm	TCÄ 4ω μl	Anthracen k'	Anthracen h, μm	Anthracen 4ω μl	Chrysen k'	Chrysen h, μm	Chrysen 4ω μl
SiO_2/nC_7	30	4,6	1,27	0,0	24,1	146,6	0,51	26,6	232,6	1,04†	29,5	330,8
SiO_2/nC_7	30,5	2,0	0,88	0,0	32,6	32,5	0,52	33,1	49,8	0,99	35,9	67,9
C_{18}/CH_3OH	30,0	1,9	0,81	0,0*	29,9	27.9	0,61	31,7	46,2	1,25	32,7	65,5
SiO_2/nC_7	30,5	1,5	1,37	0,0	24,9	16,0	0,62	25,9	26,4	1,17	26,7	35,9
C_{18}/CH_3OH	30,5	1,3	1,13	0,0*	41	15,4	0,60	41,7	24,9	1,24	41,1	34,5

* Bei den Umkehrphasen (C_{18}) war Nitromethan die inerte Probesubstanz.
† Probesubstanz: Perylen.
Probemenge: $6 \cdot 10^{-7}$ g.
Probevolumen: 1 μl.

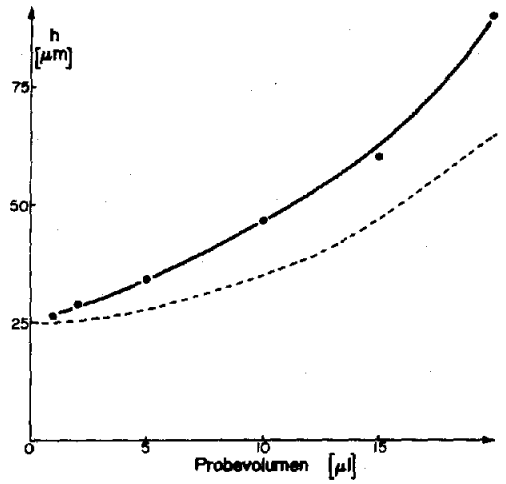

Abb. 1. Relative Bandenverbreiterung h als Funktion des Probevolumens. Ausgezogene Linie: Experimentelle Werte. Gestrichelte Linie: Nach Zitat 8 theoretisch errechnete Werte. Innendurchmesser der Säule: 1,9 mm, Länge: 30 cm, Kolonnenvolumen: 851 μl. Schleifenprobenaufgabe mit einem Schleifenvolumen von 20 μl. Stationäre Phase: C_{18}–SI 100 mit d_p = 9,8 μm, totale Porosität: 0,71. Eluent: Methanol, lineare Geschwindigkeit: 0,83 mm/sec. Probe: Nitromethan gelöst in Methanol ($k' = 0$), konstante Probemasse: 0,6 μg, Konzentration des Nitromethans in Methanol: 30–600 ppm. Zellenvolumen des UV-Detektors: 1 μl.

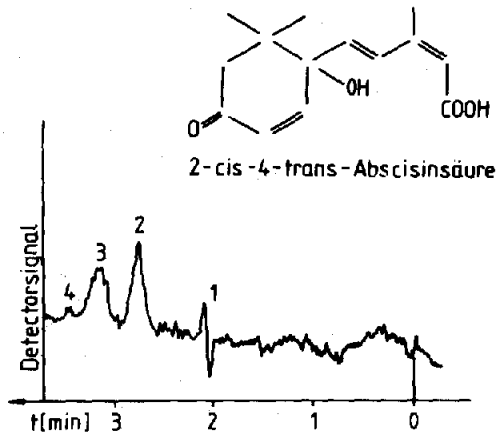

Abb. 2. Trennung von 1 ng *cis*- und *trans*-ABA in einer Säule mit 4,6 mm Innendurchmesser. 1, Inert Peak; 2, *trans*-ABA [2-*trans*-4-*trans* ABA]; 3, *cis*-ABA [2-*cis*-4-*trans* ABA]; 4, Verunreinigung. Säulenlänge: 30 cm. Eluent: Methanol/Wasser (Vol. 1:1) und 1 Gew. % Kochsalz. Umkehrphase C_{18} aus 10 μm Lichrosorb SI 100. Detektor (254 nm)-Zellenvolumen: 1 μl. Molare Extinktion von AVA bei 254 nm: *ca.* $2{,}2 \cdot 10^4$ l·mole^{-1}·cm^{-1}.

des Probevolumens aufgetragen. Wie ersichtlich nehmen die experimentell bestimmten h-Werte mit einem Faktor > 2 zu, wenn das Probevolumen von 1 auf 20 μl erhöht wird. Große Probevolumina können wünschenswert sein, wenn die Konzentration der Probesubstanz in der Probelösung sehr gering ist. In Abb. 1 wurde die auf die Kolonne injizierte Probemenge konstant gehalten, dementsprechend nahm die Konzentration des Nitromethans in der Probelösung von 600 ppm (1 μl Probevolumen) auf 30 ppm (20 μl Probevolumen) ab.

Vergleicht man die experimentell bestimmte Kurve in Abb. 1 mit den theoretisch errechneten Werten,[1,8] so ist ersichtlich, daß die experimentellen Werte nur unwesentlich höher sind als die erwarteten, wobei die Kurvenverläufe ähnlich sind.

Anwendungsbeispiel

Die Trennung der *cis*- und *trans*-Isomeren der Abscisinsäure (ABA), ist in der Botanik von Interesse. Problematisch ist die Trennung, da sowohl die zur Verfügung stehende Probemasse als auch die Konzentration der ABA in der Lösung sehr gering sind.[22]

Zuerst wurde diese Trennung an einer 4,6 mm i.D. (L = 30 cm) Säule, die mit C_{18}-Umkehrphase gepackt war, optimiert. Wie in Abb. 2 gezeigt, konnte eine Basislinientrennung erreicht werden mit einer Eluentzusammensetzung von Methanol/Wasser (1:1) mit 1% Natriumchlorid Zusatz. Auf die Säule wurde 1 μl Probe aufgegeben, die ABA-Konzentration in der Probe betrug *ca.* 1 ppm. Die aufgegebene, getrennte und nachweisbare Probemenge betrug also $1 \cdot 10^{-9}$ g. Die Nachweisgrenze von ABA konnte in diesem Experiment deswegen so niedrig gehalten werden, weil der molare Extinktionskoeffizient von ABA bei 254

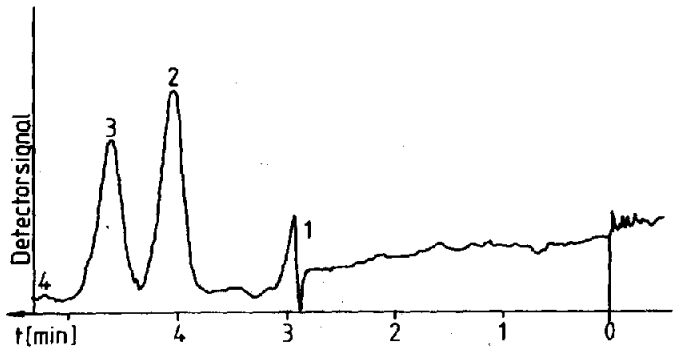

Abb. 3. Trennung von 1 ng *cis*- und *trans*-ABA in einer Säule mit 1,3 mm Innendurchmesser. Parameter wie in Abb. 2.

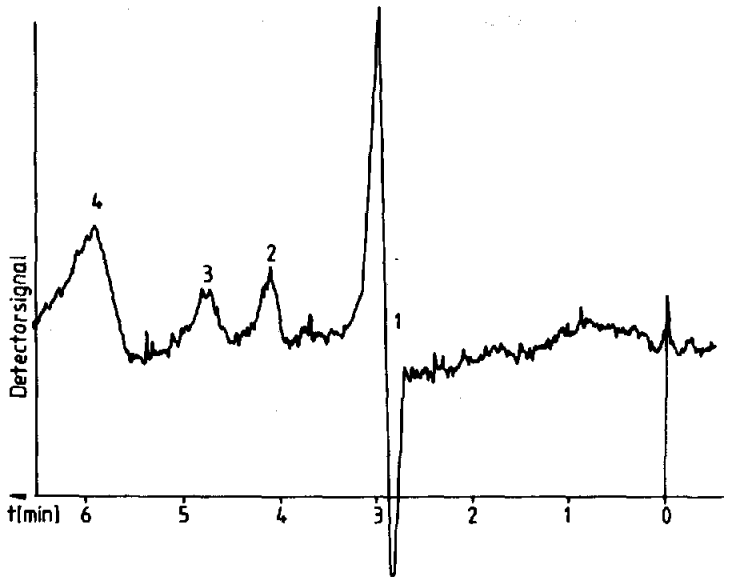

Abb. 4. Trennung von 0,1 ng *cis*- und *trans*-ABA in einer Säule mit 1,3 mm Innendurchmesser. Sonstige Parameter wie in Abb. 2.

nm etwa $22 \cdot 10^4$ $l \cdot mole^{-1} \cdot cm^{-1}$ beträgt. Die Trennung wäre nicht ungünstiger gewesen, falls man noch kleinere Probemengen mit entsprechend höheren Konzentrationen aufgegeben hätte. In Abb. 3 ist dieselbe Trennung auf einer 1,3 mm Säule gezeigt, wobei alle anderen Versuchsparameter konstant gehalten wurden. Außerdem wurde auf diese Säule ebenfalls 1 μl Probe, allerdings mit zehnmal kleinerer Konzentration aufgegeben. Die Nachweisgrenze lag hier also bei 0,1 ng. In Abb. 3 wird ein Nebeneffekt deutlich. Da die Verdünnung der aufgegebene Probe kleiner ist als in Abb. 2, erscheint als Peak Nr. 4 eine Verunreinigung. Ob diese Verunreinigung aus dem Lösungsmittel stammt oder von der Säule verdrängt wurde, soll offen gelassen werden. Die untere Nachweisgrenze zu trennender Substanzen in der Flüssigkeits-Chromatographie wird u.a. durch Verunreinigungen im Eluenten bzw. durch die Säule mitbestimmt. In Abb. 4 sind die Versuchsbedingungen wie in Abb. 3, nur die aufgegebene Probemenge beträgt (wie in Abb. 2) 1 ng.

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Summary—The dilution of the sample in liquid chromatographic columns increases with the square of the internal diameter of the tube if all other parameters are kept constant. If the mass or the volume of the sample is extremely small the separated peaks become undetectable. Irregularly packed capillary columns with an internal diameter of less than 1 mm seem to be the best solution. Unfortunately the mass of the stationary phase per unit column volume is then very small (low k'-values

and long hold-up times), and consequently the analysis time is increased, the dilution of the sample in the column becomes high and the instrumental problems are not negligible. The equipment and methods for packing glass columns with internal diameters between 1.3 and 2.0 mm are described. The columns are packed with silica gel or with reversed-phase packing (particle size ~ 10 μm), and h/d_p values between 2.5 and 4 are achieved. This ratio is more or less independent of the stationary phase and of the eluent (n-heptane or methanol). The *cis*- and *trans*-isomers of abscisinic acid are separated and detected even when the sample size is only 10^{-10} g, thanks to the high molar absorptivities.

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SIMPLE AND SENSITIVE DETERMINATION OF HEPATIC COPPER BY USE OF AN EXTRACTIVE CATALYTIC METHOD

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Summary—For determination of copper in liver tissue and in liver biopsy samples an extractive catalytic determination is proposed. After digestion of the liver samples with nitric acid, copper is extracted as the salicylate–pyridine complex into chloroform and determined catalytically directly in the organic extract by addition of ethanolic solutions of sulphanilic acid, pyridine and hydrogen peroxide. Copper can be determined in the range from 10 to 350 ppm (dry weight basis) with a relative standard deviation of 5–15%. The method enables copper to be determined in liver biopsy samples of about 5 mg dry weight by use of a simple spectrophotometer, and can be used in diagnosis of Wilson's disease.

For clinical diagnosis the estimation of trace elements in blood, urine or tissue grows in importance. Copper is one of the elements most frequently detected.

For example, early discernment of increased copper content in human liver may reveal Wilson's disease at a stage where the classical neurological symptoms have still not appeared. The normal values of copper in human liver range from 20 to 75 ppm.[1] This relatively high concentration allows the copper to be determined by all analytical methods of metal trace analysis. However, rather small samples often have to be used. Thus, in diagnosis of Wilson's disease copper has to be detected in only 10–15 mg of liver sample (wet weight) taken by biopsy.

For that reason the simple spectrophotometric methods cannot be used, and the more sensitive but also more expensive and troublesome methods, such as neutron-activation analysis[1–3] or flameless atomic-absorption spectrophotometry[4] have to be used.

To avoid the need for expensive instrumental equipment a kinetic–catalytic method has been tested for determination of copper in liver biopsy samples. This technique needs only a simple spectrophotometer as measuring instrument. The sensitivity of catalytic methods of determination is very high[5] and their lack of selectivity can be overcome by combination of the catalytic determination with a suitable separation step.[6]

The method chosen is based on the catalytic effect of copper on the oxidation of sulphanilic acid with hydrogen peroxide in presence of pyridine as activator.[7] The absorbance of the reaction system is measured at 370 nm after 30 min (fixed-time method). The absorbance of the oxidation products of sulphanilic acid is directly correlated with the copper concentration.

The copper can be separated from the matrix by preliminary extraction of the mixed pyridine–salicylate complex into chloroform.[8]

Liver biopsy samples of about 5 mg dry weight are mineralized with nitric acid, the residue is dissolved by use of the extracting agents and the copper extracted into chloroform. After dilution of the extract with ethanolic reagent solutions, copper in the range from 10 to 350 ppm (dry weight) can be determined.

EXPERIMENTAL

Reagents

All reagents were analytical grade. Redistilled water and 96% ethanol were used throughout the work. For mineralization of samples concentrated nitric acid (65% HNO_3, Suprapur, Merck, FRG) and fuming nitric acid (98–100% HNO_3, VEB Feinchemie Sebnitz, GDR) were used.

Sulphanilic acid (0.02M)/pyridine (0.6M) solution (A). In a 50-ml standard flask dissolve 173 mg of sulphanilic acid and 2.4 ml of pyridine in ethanol by shaking and heating on a water-bath. Cool, then dilute the solution to 50 ml with ethanol. The solution is stable for 2 weeks.

Hydrogen peroxide solution (0.44M). Prepare by dilution of 30% hydrogen peroxide solution to 50 ml with ethanol. Analyse by permanganate titration.

Copper(II) standard solution (0.01M). Dissolve 170 mg of $CuCl_2.H_2O$ in 100 ml of water and standardize by EDTA titration with PAN as indicator.[9]

Salicylate (0.1M)/pyridine (0.1M)/fluoride (0.8M) solution (B). In a 250-ml standard flask dissolve 4.0 g of sodium salicylate, 8.4 g of sodium fluoride and 2.0 ml of pyridine in about 200 ml of water. Adjust the pH to 6.3 and dilute to 250 ml. Filter before use, if necessary.

Apparatus

Liver samples in the lower milligram range were weighed on a Sartorius electronic microbalance.

A "Spekol" spectrophotometer equipped with a temperature-controlled cell holder was used.

Copper was determined by flameless atomic-absorption spectrophotometry with a Jarrel–Ash double-beam dual-channel atomic-absorption spectrophotometer type 811 equipped with a Fisher microthermal atomizer MTA 2. Tantalum ribbon was used as sample holder.

Tissue processing

Deep-frozen liver samples were sliced thin by a scalpel and dried at 100° for 15 hr. About 150 mg of the dried liver were placed in a porcelain crucible on a hot-plate and about 5 ml of concentrated nitric acid were added dropwise until a white residue with dark patches was obtained. Mineralization was completed by stepwise addition of about 2 ml of fuming nitric acid. The white residue was dissolved in about 5 ml of 5% hydrochloric acid with warming. After cooling, the solution was made up to 50 ml. Aliquots of the solution were used for analysis.

Extractive catalytic determination

In a separatory funnel up to 2 ml of sample solution and 2 ml of solution *B* were made up to 4 ml with water. Then the aqueous solution was shaken with 4 ml of chloroform for about 3 min. After separation of the organic phase 2.40 ml of the chloroform extract were put into a test-tube together with 3.60 ml of hydrogen peroxide solution. The mixture was put in a thermostat at 45° for 10 min and then the reaction was started by addition of 2 ml of solution *A* (also at 45°) and mixing by shaking the test-tube. The reaction was left to proceed for 30 min at 45° and was stopped by cooling the reaction vessel in a water-bath (20) for 5 min. The solution was transferred to a 50-mm cell and the absorbance measured at 370 nm.

The difference in absorbance between the blank and the sample was a direct measure for the copper concentration.

The absorbance of the blanks, measured against water, was about 0.24. These relatively high values were not produced by impurities in the reagents but resulted from the uncatalysed reaction.

Analysis of liver biopsy samples

In a porcelain crucible on a hot-plate 3–8 mg of dried liver or liver from a biopsy were dissolved by addition of 0.2 ml of concentrated nitric acid. After addition of some drops of fuming nitric acid a white residue was obtained. For complete mineralization the samples were kept in a muffle furnace at 550° overnight. The residue was dissolved with 1.5 ml of hot water and 1.5 ml of solution *B*. The solution was carefully transferred to a 25-ml separatory funnel and shaken with 3 ml of chloroform for 3 min. Then a mixture of 1.2 ml of chloroform extract with 1.8 ml of hydrogen peroxide solution in a test-tube was placed in the thermostat at 45° for 10 min. Then 1 ml of solution *A* (at 45°) was added, and the reaction started by shaking the test-tube. After reaction for 30 min at 45° the solution was cooled and the absorbance measured as described above.

Atomic-absorption measurements

For atomization, solutions of digested liver samples were diluted to give a final hydrochloric acid concentration of 0.01*M* and put directly on the tantalum ribbon by micropipette. The most suitable parameters for the copper determination are listed in Table 1.

Table 1. Working conditions for flameless atomic-absorption spectroscopic determination of copper

Resonance line	324.7 nm (channel A)
Background correction	323.0 nm (channel B)
Lamp current	10 mA (Jarrel–Ash zinc lamp)
Gas flow-rate	Argon 390 l./hr and "H, 2" for hydrogen
Drying step	30 sec at 130°C
Ashing step	24 sec at 700°C
Atomization	2 sec at 1650°C
Sample volume	10 μl

RESULTS

For reproducible results to be obtained, the copper has to be completely freed from the organic matrix. For that reason mineralization of liver is a necessary preliminary to the catalytic determination. The best results are obtained if both concentrated and fuming nitric acid are used.

After digestion the residue is dissolved in dilute hydrochloric acid and the copper is extracted into chloroform after addition of salicylate and pyridine. (For analysis of liver biopsy samples the residue is dissolved in the extracting agent solution alone; the chloroform phase with the extracted copper is then used directly for the catalytic determination by dilution with the ethanolic reagent solutions.) The calibration curve for copper is linear in the range from 5 to 100 ng/ml (Fig. 1, curve C_1).

The only interference results from the relatively high content of iron in liver tissues. With salicylate iron forms a stable red complex which is partially extracted into the chloroform phase and does interfere with the catalytic determination.

In order to eliminate this interference sodium fluoride was tested as masking agent for iron(III). Fluoride up to a concentration of 0.5*M* has no influence on the extraction catalytic procedure. For the analysis a fluoride concentration of 0.4*M* was used, which produces a constant ionic strength and binds up to 10% of iron in the liver (dry weight) (the usual iron content[10] is about 0.06%, dry weight).

The accuracy of the method was checked by systematic investigations[11] as well as by independent determinations by atomic-absorption spectrophotometry.

The existence of a constant systematic error was tested for by determination of copper in different amounts of calf liver. The error calculated (Table 2) was found to be statistically not significant,[11] which

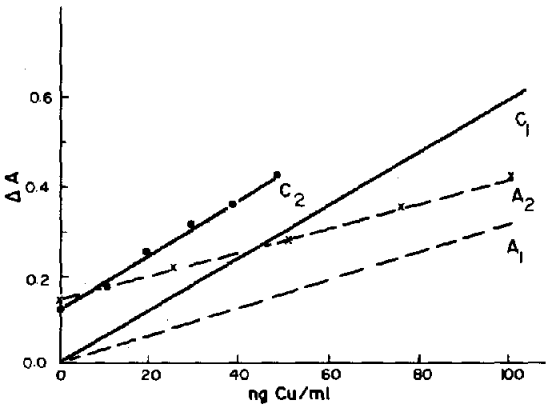

Fig. 1. Calibration graphs for extractive catalytic and AAS determinations of copper in aqueous solution and in calf liver. Extractive catalytic determination: C_1—aqueous solution ($b = 6.06 \times 10^{-3}$ ml/ng); C_2—calf liver. AAS determination: A_1—without matrix ($b = 3.1 \times 10^{-3}$ ml/ng); A_2—calf liver.

Table 2. Results of copper determination in calf liver

	Extraction catalytic method	AAS
Constant error[11], [Cu], *ng/ml*	0.8	26.2
Proportional error[11]	1.00	0.84
Sensitivity, *b*,† *ml/ng*	6.06×10^{-3}	2.6×10^{-3}
Mean content*, $\bar{x}$, *ppm*	103	107
Number of determinations	12	17
Standard deviation, *S*, *ppm*	8.7	16
Coefficient of variation, $S\ 100/\bar{x}$, %	8.5	15

* Refers to dried liver.

† According to the calibration function $\Delta A = b[\text{Cu}] + a$ where [Cu] B in ng/ml and A is the intercept of the regression line.

Table 3. Extractive catalytic determination in biopsy samples of human liver

Sample	Dry weight used, *mg*	ΔA*	[Cu], *ppm*
1	Blank	−0.004	—
2	4.82	0.227	77.1 ± 3.2
3	8.27	0.270	53.9 ± 2.0
4	4.14	0.116	46.4 ± 2.0
5	4.54	0.155	57.4 ± 3.7
6	4.46	0.488	192.0 ± 3.7

* Duplicate determinations.

means that there is no proof of the existence of a constant error.

To evaluate any proportional systematic error,[11] calf-liver samples were spiked with known amounts of copper before the digestion procedure, and the slope of the resulting calibration curve was compared with that for aqueous solutions containing the same amounts of added copper. The slopes were identical (Fig. 1, curves C_1 and C_2), establishing that there is no proportional error. Thus the extraction catalytic procedure can be used without recourse to the standard-addition method.

The catalytically determined copper content in calf liver was in agreement with the value obtained by AAS determinations (Table 2), but the AAS results had both a constant and a proportional error (Table 2 and Fig. 1 curves A_1 and A_2).

The standard deviation of extractive catalytic determinations in calf (Table 2) and human liver (Table 3) was found to vary from about 5 to 10 ppm Cu. Depending on the sample weight and the copper content the coefficient of variation is between 5 and 15% (*cf.* Tables 2 and 3).

The limit of detection was calculated according to the 3*s*-criterion[11] on the basis of the standard deviation of 14 blanks measured during a two-month period. The limit of detection was 5 ng of Cu per ml, which allows down to 10 ppm of copper to be determined in 5 mg of dried liver.

Because of the high sensitivity the method was used for copper determination in biopsy samples.

By use of Menghini needles biopsy samples of about 10–15 mg of wet liver were obtained. The weight loss on drying was about 70%, *i.e.*, about 5 mg of dried liver was available for determination of copper, which was adequate for use with modified procedure.

The results for normal persons (1–5) and for one patient (6) suspected to have Wilson's disease are presented in Table 3. The coefficient of variation of the determinations was established by duplicate analysis of 4 different portions of liver from sample No. 4 (Table 3) and found to be 12.7%.

These copper concentrations in human liver are relatively high compared to those reported in the literature[1–4] but still in a range which is described as normal by many authors (*e.g.*, 12–75 ppm, dry weight[1]).

DISCUSSION

The determination of copper in biopsy samples by use of conventional spectrophotometry is scarcely possible, because the sensitivity of the common reagents is too low, *e.g.*, neocuproine ($\epsilon = 7.9 \times 10^3$ $1.\text{mole}^{-1}.\text{cm}^{-1}$)[7] or bathophenanthroline ($\epsilon = 1.3 \times 10^4$ $1.\text{mole}^{-1}.\text{cm}^{-1}$).[12] The sensitivity of the extractive catalytic procedure is 5–10 times greater ($\epsilon = 7.6 \times 10^4$ $1.\text{mole}^{-1}.\text{cm}^{-1}$), which makes the

Table 4. Comparison of different methods for determination of copper in human liver biopsy samples

Parameter	Neutron-activation[1]	Flameless AAS	Extractive catalytic method
Concentration range*, *ppm*	5–700	10–100	10–350
Amount of liver necessary for analysis, *mg*	0.4	1	5
Coefficient of variation, %	10–12	9–15	10–15
Pretreatment of sample	Mineralization (ion-exchange)	Mineralization	Mineralization, extraction

* Refers to dry weight.

method applicable for analysis of liver biopsy samples for copper.

Of course, the sensitivity cannot compete with that of methods such as neutron-activation analysis[1-3] and flameless atomic-absorption spectroscopy[4] but the procedure has the advantage of needing only a simple spectrophotometer and allows copper to be determined in duplicate in 5 mg of dried liver samples over the clinically interesting range from 10 to 100 ppm or higher.

A comparison of methods according to the most important parameters is presented in Table 4.

The extractive catalytic method is now being tested for routine analysis in diagnosis of Wilson's disease, which should be suspected if the copper content is in the range 150–250 ppm. Because the reproducibility improves with increasing copper content, duplicate determinations are adequate for reliable diagnosis.

Acknowledgement—We would like to thank Doc. Dr. H. Willgerodt from the children's hospital of the Karl-Marx-University, Leipzig, for placing the liver samples at our disposal, as well as for helpful discussions.

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UNTERSUCHUNGEN ZUR INDIREKTEN MECHANISIERTEN KATALYTISCH-SPEKTRALPHOTOMETRISCHEN BESTIMMUNG VON α-AMINOPOLYCARBONSÄUREN UND PHOSPHATEN

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Zusammenfassung—α-Aminopolycarbonsäuren und kondensierte Phosphate inhibieren die Fe-katalysierte Oxydation von *p*-Phenetidin mit Wasserstoffperoxid. Mittels eines Durchflußanalysators wurden die Inhibitorwirkung von sieben α-Aminopolycarbonsäuren und technisch wichtigen Phosphaten untersucht und die Ergebnisse komplexchemisch interpretiert. Eine mechanisierte Bestimmung ist für einige α-Aminopolycarbonsäuren (Tetra-, Penta- und Hexasäuren) im Konzentrationsbereich von $2{,}5 \cdot 10^{-7}$ bis $2{,}5 \cdot 10^{-6}$ *M* bei guter Reproduzierbarkeit (relative Standardabweichungen im mittleren Konzentrationsbereich um ±2%) möglich.

Die Notwendigkeit der Bestimmung von synthetischen α-Aminopolycarbonsäuren und kondensierten Phosphaten ergibt sich in immer breiterem Maße durch den zunehmenden Einsatz dieser Produkte in der Industrie, der Land- und Hauswirtschaft sowie in der Medizin. Dabei muß die Analytik neben einer Überwachungsfunktion beim Herstellungsprozeß (Prozeßkontrolle) auch eine Kontrollfunktion in umweltrelevanten Bereichen übernehmen. Gelangen z.B. α-Aminopolycarbonsäuren oder ihre Metallkomplexe unkontrolliert in die Umwelt, können Störungen des Ökosystems auftreten, da durch die Wechselwirkung Metall-Ligand die Wanderung von Metallen im Geo- und Biozyklus wesentlich beeinflußt wird.[1]

Von den α-Aminopolycarbonsäuren werden technisch als Ersatz von Polyphosphaten in Waschmitteln vor allem Äthylendiamintetraessigsäure (ÄDTE) und Nitrilotriessigsäure (NTE) als Sequestrierungsmittel angewendet. Eine umfassende Übersicht über das breite Applikationsspektrum der synthetischen anorganischen und organischen Komplexbildner gibt die Monographie von Chaberek und Martell.[2]

Als Konsequenz der vielfältigen Verwendung wurden zahlreiche Analysenmethoden zur Bestimmung synthetischer Komplexbildner für die einzelnen Anwendungsgebiete und für die Umweltüberwachung entwickelt. Dabei dominieren chemische Analysenverfahren in Verbindung mit Trennoperationen.

Besonders die Bestimmung von Sequestrierungsmitteln in umweltrelevanten Matrices erfordert wegen der hohen Probenzahlen und des damit verbundenen Arbeitsaufwandes die Anwendung einer weitgehend mechanisierten Analysenmeßtechnik.

Bisher sind aber nur wenige mechanisiert ausgeführte Bestimmungen für α-Aminopolycarbonsäuren bzw. Polyphosphate bekannt.

Eine recht nachweisstarke Methode (Doppelzellen-Gleichstrom-Oszillopolarographie) zur Bestimmung von NTE in natürlichen Wässern, Abwässern und Detergentien wird von Afghan und Mitarbeitern[3] vorgeschlagen. Die Anwendbarkeit dieser Methode wird jedoch durch die aufwendige Detektoreinheit begrenzt. Eine photometrische Bestimmung für 0,25 bis 1%ige NTE-Lösungen wird von Vanwelssenaeres und Clinckemaillie[4] beschrieben. Eine photometrisch indizierte Metallverdrängungsreaktion zur Bestimmung von NTE im Bereich von 1 bis 10 mg NTE/l ist in einer Übersicht automatisierter Methoden zur Wasserqualitätskontrolle von DuCros und Salpeter[5] erwähnt.

Ziel unserer Untersuchungen war es, eine empfindliche mechanisierte Bestimmungsmethode für Sequestrierungsmittel auszuarbeiten, die sich mit vertretbarem apparativen Aufwand mechanisieren läßt. Unter dem Gesichtspunkt einer Spurenbestimmung in Lösung sind wegen ihres hohen Nachweisvermögens auch kinetisch-katalytische Analysenmethoden interessant. Dabei kann sowohl ein aktivierender als auch ein inhibierender Einfluß der zu bestimmenden Komplexbildner auf das Katalyseverhalten von Metallkatalysatoren ausgenutzt werden. Übersichten über Arbeiten auf diesem Gebiet wurden u.a. von Motola,[6] Müller und Werner[7] und Greinke und Mark[8] referiert.

Zur kinetisch-katalytischen Bestimmung von α-Aminopolycarbonsäuren und kondensierten Phosphaten wurde in der vorliegenden Arbeit der Inhibitoreffekt dieser Verbindungen auf die Fe-katalysierte und durch 1,10-Phenanthrolin aktivierte Redoxreaktion zwischen *p*-Phenetidin und Wasserstoffperoxid[9] genutzt. Eine Anwendung dieser Indikatorreaktion zur indirekten kinetisch-katalytischen Bestimmung von Komplexbildnern sollte sehr geeignet sein, weil

(*i*) Eisen(III) mit α-Aminopolycarbonsäuren und Phosphaten sehr stabile Komplexe bildet,

(*ii*) die Indikatorreaktion sehr nachweisstark auf Eisen ist und damit empfindliche Bestimmungsmethoden für Komplexbildner zu erwarten waren,

(*iii*) der Aktivator 1,10-Phenanthrolin durch Konkurrenzreaktion mit dem Katalysator Eisen die Inhibitorwirkung der unterschiedlichen Komplexbildner abstufen kann.

Eine mechanistische Deutung der Fe-katalysierten Reaktion zwischen *p*-Phenetidin und H_2O_2 wird von Bontchev[10] wie folgt gegeben:

$$M + S \xrightarrow{k_1} M' + S' \qquad (1)$$

$$S' \longrightarrow P \qquad (2)$$

$$M' + B \xrightarrow{k_2} M + Red \qquad (3)$$

mit M/M' = Katalysator in der oxydierten bzw. reduzierten Form; S = *p*-Phenetidin; P = Oxydationsprodukt des Substrates; B = H_2O_2.

Die Wirkung des Aktivators 1,10-Phenanthrolin wird dabei durch die Komplexbildung mit M' und der dadurch bewirkten Verschiebung des Gleichgewichtes in Gleichung 1 nach rechts erklärt.

In Anwesenheit eines Liganden L (zu bestimmender Komplexbildner) muß (bei Annahme einer 1:1-Komplexbildung) noch der Schritt

$$M + L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} ML \qquad (4)$$

berücksichtigt werden.

Allgemeine Betrachtungen zur Inhibitorwirkung von Liganden

Der in der Lösung vorliegende Ligand L bildet mit dem Katalysator M eine Komplexverbindung ML. Dieser Komplex kann entweder katalytisch inaktiv sein (Vollinhibition) oder seine katalytischen Eigenschaften unterscheiden sich von den katalytischen Eigenschaften des Ausgangskatalysators (Teilinhibition). Betrachtet man den einfachsten Fall der Vollinhibition und zieht zu ihrer allgemeinen Erklärung die von Yatsimirskii[11] in die formal-kinetische Behandlung homogen katalysierter Reaktionen eingeführte Graphentheorie heran, können die Reaktionen (1), (3) und (4) durch folgenden Graph (Abb. 1) repräsentiert werden. Die Geschwindigkeit der Gesamtreaktion ergibt sich dann bei Anwendung der Bilanzgleichung von Meson und Zimmermann[12] zu

$$v = \frac{k_1 k_2 [S][B] C_K}{k_1[S] + k_2[B] + K[B][L]k_2} \qquad (5)$$

mit $K = k_3/k_{-3} = K_{ML}$; C_K = Gesamtkonzentration des Katalysators = ([M] + [M'] + [ML]).

Diese Gleichung zeigt die Abhängigkeit der Inhibitorwirkung eines Liganden L von der Komplexstabilitätskonstanten K_{ML}. Geht K_{ML} gegen Null, so geht Gleichung (5) in die Geschwindigkeitsgleichung für die nicht-inhibierte Reaktion

$$v = \frac{k_1 k_2 [S][B] C_K}{k_1[S] + k_2[B]} \qquad (6)$$

über und der Knoten ML im Graphen der Abbildung 1 verschwindet. Wächst dagegen K_{ML} an, so wird auch der Nenner des Bruches in Gleichung (5) größer und die katalysierte Reaktion kommt zum Stillstand. Bei sehr großen Werten von K_{ML} werden schon äquimolare Mengen eines Liganden in bezug auf den Katalysator die Reaktion vollständig stoppen, bei entsprechend höheren Konzentrationen an Inhibitor können auch nicht so "starke" Liganden einen Reaktionsstillstand bewirken.

Die Verringerung der katalytischen Aktivität eines Katalysators durch Komplexbildung mit einem Liganden L ermöglicht zwei Aussagen:

(*i*) die Abnahme der katalytischen Aktivität ist eine Funktion der Konzentration des Inhibitors und gestattet dadurch dessen Bestimmung;

(*ii*) beim Vergleich unterschiedlicher Inhibitoren gleicher Konzentration ist die Abnahme der katalytischen Aktivität ein Maß für die Stärke der Wechselwirkung Katalysator-Inhibitor und ermöglicht, vergleichende Aussagen über die Komplexbildung (Größe von K_{ML}) zu machen (siehe dazu auch Zitat 13).

Die Voraussetzung für diese allgemeinen Betrachtungen, daß die gebildeten Komplexe katalytisch nicht aktiv sind (Vollinhibition) bestätigte sich in den weiteren Experimenten. Dies ist nicht überraschend, da sowohl die mehrzähnigen α-Aminopolycarbonsäuren als auch die Phosphate und Polyphosphate den Katalysator in der Regel koordinativ sättigen und ihn so gegen Wechselwirkungen mit den Reaktanten der Indikatorreaktion abschirmen.

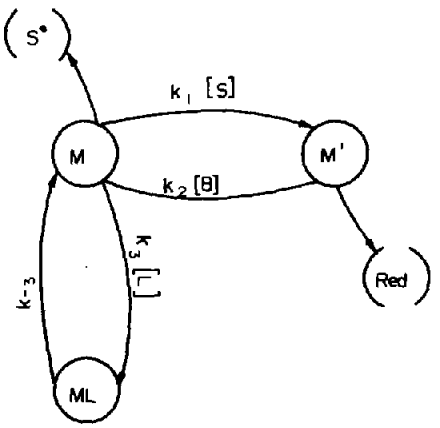

Abb. 1. Graph für den Ablauf der Fe-katalysierten Reaktion zwischen *p*-Phenetidin und H_2O_2 in Anwesenheit eines Inhibitors L.

EXPERIMENTELLER TEIL

Geräte und Versuchsauswertung

Alle Glasgeräte wurden durch Chromschwefelsäure und mehrfaches Spülen mit bidestilliertem Wasser gereinigt. Die Untersuchungen und Bestimmungen wurden mit einem Durchflußanalysator "Kontinuierlicher Analysenautomat" des VEB MLW Prüfgerätewerk Medingen, Sitz Freital, DDR, durchgeführt (siehe dazu auch Zitat 14). Die entsprechenden Versuchsparameter sind dem Fließschema in Abb. 2 zu entnehmen. Experimentell erfolgte die Bestimmung der Inhibitorwirkung und -konzentration über Extinktionsänderungen pro Zeit, die aus den unterschiedlichen Bildungsgeschwindigkeiten des Reaktionsproduktes der Indikatorreaktion in An- bzw. Abwesenheit der inhibierend wirkenden Liganden (weniger oder mehr katalysierend wirkendes "freies" Eisen) resultieren. Voraussetzung für eine einfache Auswertung ist, daß die verschiedenen Inhibitoren nur eine Komplexierung (Bildung von ML) bewirken, den Wirkmechanismus (Gleichung 1 bis 3) aber nicht verändern. Die Wechselwirkung zwischen Katalysator und Ligand wird graphisch dargestellt, indem man die Restkonzentration an katalytisch wirkendem Eisen (ermittelt aus dem Extinktions–Zeit-Verlauf der Indikatorreaktion) gegen die Inhibitorkonzentration aufträgt. Da jede Extinktionsänderung einer definierten Konzentration an katalytisch wirksamen Eisen entspricht, können die ermittelten Werte mittels entsprechender Eichkurven in (Eisen)-Konzentrationswerte transformiert werden. In einem Koordinatensystem mit der Konzentration an katalytisch aktivem Eisen (Fe^*, siehe Abb. 3 und 4) als Ordinaten- und der Ligandkonzentration als Abszissenwert liefert der Schnittpunkt der Kurve mit der Ordinatenachse dann den Konzentrationswert des reinen Eisenstandards (bei allen Versuchen $2{,}5 \cdot 10^{-6}$ *M*).

Versuchsdurchführung

Zur Aufnahme von Eichkurven werden 0,1 ml der Eisenstammlösung ($2{,}5 \cdot 10^{-4}$ *M*) in einem 10-ml Maßkölbchen mit steigenden Mengen an Inhibitorlösung versetzt, mit Wasser auf 10 ml aufgefüllt und die katalytisch noch wirksame Eisenkonzentration mit dem Durchflußanalysator (über die Extinktionsänderung bei konstanter Zeit) ermittelt. Alle weiteren Manipulationen wie Proben- und Reagenziendosierung, Vermischen der Reaktanten, Inkubation des Reaktionsansatzes und photometrische Indikation der Reaktionsprodukte erfolgen durch den Analysator analog einer früher beschriebenen Eisenbestimmung im Trinkwasser.[24]

Eine nicht-mechanisierte spektralphotometrische Ermittlung der Reaktionsgeschwindigkeit der Indikatorreaktion und daraus über das katalytisch noch wirksame Eisen der Inhibitorkonzentration ist nach Zugabe der entsprechenden Reaktanten zur Untersuchungslösung und Starten der Reaktion mit H_2O_2-Lösung ebenfalls möglich (siehe dazu z.B. Zitat 9).

Reagenzien und Probelösungen

p-Phenetidin-HCl, 1,4%ige Lösung (täglich frisch zubereitet). *p*-Phenetidin-HCl wurde aus frisch destilliertem (Vakuum, Stickstoffatmosphäre) *p*-Phenetidin und Salzsäure erhalten. In einer braunen Flasche aufbewahrt, ist es über Monate haltbar.

1,10-Phenanthrolin-HCl-H_2O. Stammlösung $1{,}1 \cdot 10^{-2}$*M*, Arbeitslösung $1{,}1 \cdot 10^{-3}$*M* (täglich frisch zubereitet).

Wasserstoffperoxid, 0,3M. Gehalt permanganometrisch bestimmt.

Puffer. Nach Clark und Lubbs, pH = 2,8: 51,08 g Kaliumhydrogenphthalat (reinst), zweimal umkristallisiert, in *ca.* 2 l Wasser lösen, 1325 ml 0,2*M* Salzsäure zugeben und auf 5 l auffüllen.

Spüllösung, 0.01M *Salzsäure.*

$FeCl_3$-Lösung. Aus einer $5 \cdot 10^{-2}$*M* Lösung in 0,5*M* Salzsäure wurde täglich die $2{,}5 \cdot 10^{-4}$*M* Arbeitslösung sowie andere benötigte Standardlösungen in 1*M* Salzsäure hergestellt.

Die Stammlösungen der α-Aminopolycarbonsäuren sowie der Phosphate wurden durch Auflösen der entspre-

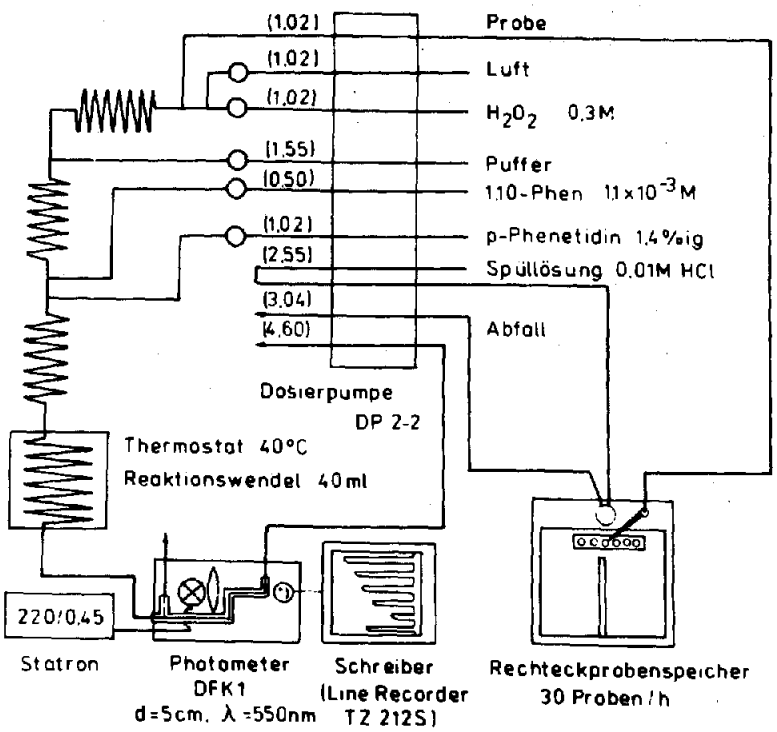

Abb. 2. Fließschema zur mechanisierten katalytischen Eisenbestimmung mittels der *p*-Phenetidin-H_2O_2-Reaktion. In Klammern Förderleistung in ml/min.

chenden Handels- und Laborpräparate bzw. der technischen Produkte in Wasser erhalten. Die Stammlösungen der α-Aminopolycarbonsäuren wurden in Polyäthylenflaschen aufbewahrt, die Konzentration wöchentlich potentiometrisch überprüft.

Die Lösungen der kondensierten Phosphate wurden täglich frisch zubereitet. Eine Gehaltsbestimmung der Phosphatlösungen erfolgte durch pH-Messungen von 1,0%igen Stammlösungen, die mit Literaturwerten[15] verglichen wurden.

α-Aminopolycarbonsäuren

Iminodiessigsäure (IDE), $10^{-2}M$.
N-Hydroxyäthyleniminodiessigsäure (HIDE), $5 \cdot 10^{-3}M$.
2-Aminocyclohexanol-*N*,*N*-diessigsäure (ACDE), $5 \cdot 10^{-3}M$.
Nitrilotriessigsäure (NTE), $5 \cdot 10^{-3}M$.
Äthylendiamintetraessigsäure (ÄDTE), $5 \cdot 10^{-2}M$.
1,2-Diaminocyclohexantetraessigsäure (DCTE), $1 \cdot 10^{-2}M$.
Diäthylentriaminpentaessigsäure (DTPE), $2 \cdot 10^{-2}M$.
Triäthylentetraminhexaessigsäure (TTHE), $2 \cdot 10^{-3}M$.

Phosphate und Polyphosphate

Natriumdihydrogenphosphat, NaH_2PO_4, 0,1*M*.
Tetranatriumdiphosphat (reinst), $Na_4P_2O_7$, 0,0175*M*.
Pentanatriumtriphosphat (PTP), technisch, $Na_5P_3O_{10}$, 1%ige Lösung.
Grahamsches Salz, technisch, 1%ige Lösung.
Metaphosphorsäure, HPO_3, 35%ig.
Natriummetaphosphat, $NaPO_3$, 1%ige Lösung.

(Herrn Prof. Dr. E. Hoyer, Sektion Chemie der Karl-Marx-Universität, Leipzig, danken wir für die Überlassung einiger α-Aminopolycarbonsäuren, dem VEB Stickstoffwerke Piesteritz, DDR, für die Bereitstellung von technischen Phosphaten).

ERGEBNISSE UND DISKUSSION

Die Komplexchemie der α-Aminopolycarbonsäuren und der Phosphate ist in der Literatur breit behandelt worden.[17–22] In dieser Arbeit sollen deshalb nur die wichtigsten und analytisch relevanten Ergebnisse unserer Untersuchungen diskutiert werden. Eine ausführliche komplexchemische Interpretation aller Untersuchungsbefunde wird von Schurig[23] vorgenommen.

Unter Berücksichtigung aller Wechselwirkungen des Katalysators mit den potentiellen Liganden in der Lösung (1,10-Phenanthrolin, Chloridionen, Wasser, *p*-Phenetidin, Reaktionsprodukte, H_2O_2 u.a.) ergab sich, daß bei einer konditionellen Stabilitätskonstanten der Metall-Inhibitor-Komplexe $K_{M \cdot L} \geq 2 \cdot 10^{10}$ Reaktionsstillstand schon bei einem äquimolaren Verhältnis des Liganden zum Metall einsetzt. Komplexbildner wie ÄDTE, DTPE, DCTE und TTAHE erfüllen diese Bedingung, bei den anderen untersuchten Inhibitoren wird bei einem äquimolaren Ligand-Metall-Verhältnis nur eine teilweise Inhibition beobachtet (Abb. 3).

Bei den Diessigsäuren kann nur bei einem hohen Überschuß eine weitgehende Inhibition der katalytischen Aktivität des Eisens beobachtet werden. Zwischen der Abnahme der katalytischen Aktivität des Eisenstandards und der Ligandkonzentration besteht keine Linearität, so daß eine analytische Auswertung mit einer einfachen Auswertetechnik nicht möglich ist. Wie Abbildung 3 zeigt, besteht für die NTE im Konzentrationsbereich von 0,5 bis $2{,}5 \cdot 10^{-6}M$ NTE eine strenge lineare Abhängigkeit zwischen der Inhibitorwirkung und der Konzentration, die zu einer Gehaltsbestimmung genutzt werden kann. Proben höherer Konzentration verdünnt man entsprechend, um im linearen Bereich arbeiten zu können. In diesem Fall sind dann für eine Bestimmung mindestens zwei Ansätze erforderlich.

Die ÄDTE, DCTE, DTPE und TTAHE komplexieren das im Reaktionsgemisch vorliegende Eisen infolge der hohen konditionellen Stabilitätskonstanten $K_{M \cdot L}$ bei äquimolaren Verhältnissen vollständig. In einem Konzentrationsbereich von 0,25 bis $2{,}5 \cdot 10^{-6}M$ α-Aminopolycarbonsäure besteht ein linearer Zusammenhang, der quantitative Bestimmungen ermöglicht (Tab. 1).

Aus den Untersuchungsergebnissen (Abb. 3) geht hervor, daß TTHE neben einem 1:1-Komplex in der Reaktionsmischung noch einen Zweikernkomplex bil-

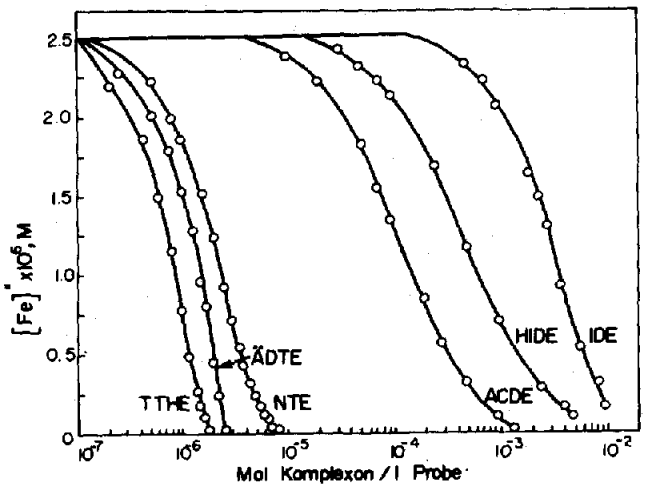

Abb. 3. Übersicht über die Inhibitorwirkung von α-Aminopolycarbonsäuren auf die Fe-katalysierte Reaktion zwischen *p*-Phenetidin und H_2O_2: DCTE, DTPE und TTAHE wie ÄDTE.

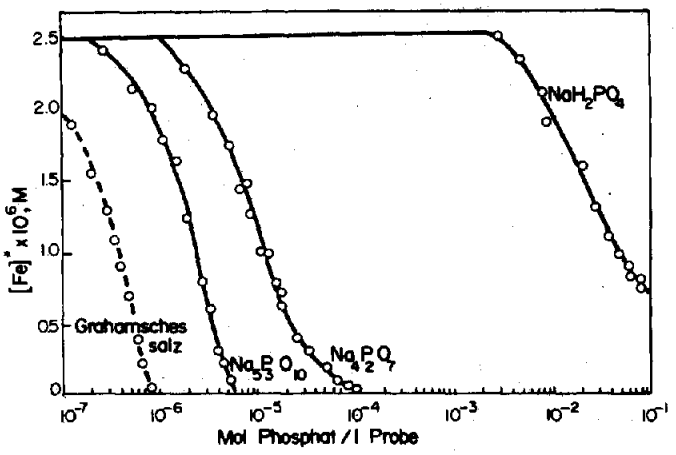

Abb. 4. Übersicht über die Inhibitorwirkung von Phosphaten auf die Fe-katalysierte Reaktion zwischen *p*-Phenetidin und H_2O_2.

det. Auch hier ist, ähnlich wie bei der NTE, nur der lineare Teil zwischen 0,2 und $2{,}5 \cdot 10^{-6} M$ TTHE analytisch auswertbar.

Die Reaktionshemmung durch Orthophosphat, Pyrophosphat und Triphosphat (Abb. 4) kann als teilweise Inhibition im Sinne einer unvollständigen Komplexbildung aufgrund der zu geringen konditionellen Stabilitätskonstanten der Eisen-Phosphat-Komplexe gedeutet werden. Die Einordnung des Inhibitionseffektes des Grahamschen Salzes und des Metaphosphates ist problematisch, da über das Molekulargewicht und somit über die Anzahl der möglichen Koordinationsstellen für die beiden Verbindungen keine genauen Angaben vorliegen. Von den untersuchten Phosphaten existiert nur für das Pentanatriumtriphosphat (PTP) ein linearer Zusammenhang zwischen der Inhibitorkonzentration von 0,27 bis $2{,}7 \cdot 10^{-6} M$ und der freien, katalytisch aktiven Eisenkonzentration. Die erhaltene Kurve (Abb. 4) ist mit der von NTE praktisch identisch. Eine Hydrolyse des PTP zum Orthophosphat ist unter den gewählten experimentellen Bedingungen nicht zu erwarten, da die Halbwertszeit für PTP bei pH = 2 (Arbeits-pH-Wert) und 25° *ca.* 700 Stunden beträgt. Für die anderen Phosphate sind spezifische Eichkurven notwendig, die aber durch ihren gekrümmten Verlauf die praktische Auswendung stark einschränken.

Die gewählte Indikatorreaktion (Fe-katalysierte Oxydation von *p*-Phenetidin mit Wasserstoffperoxid) ist für die Bestimmung von Tri- bis Hexa-α-Aminopolycarbonsäuren geeignet. Der funktionale Zusammenhang zwischen der Inhibitorkonzentration und der Reaktionsgeschwindigkeit (ausgewertet über die katalytisch noch wirksame Eisenkonzentration) ist in Form von Geradengleichungen, die mittels linearer Regression errechnet wurden, in Tabelle 1 zusammengefaßt.

Die relativen Standardabweichungen der Bestimmungen liegen für alle α-Aminopolycarbonsäuren bei ±2% von der unteren Grenze des Arbeitsbereiches bis zu mittleren Konzentrationen. Für $2{,}25 \cdot 10^{-6} M$ ÄDTE, DCTE, DTPE und TTAHE muß man mit relativen Fehlern zwischen 10 und 20% rechnen. Das Arbeiten an der oberen Grenze ($2{,}5 \cdot 10^{-6} M$) sollte man vermeiden, weil dann das katalytisch wirkende Eisen fast vollständig komplexiert ist und sich dadurch äußerst geringe Extinktionsänderungen ergeben, die in der Nähe der Blindwerte liegen.

Die ausgearbeiteten mechanisierten Bestimmungsmethoden sind für α-Aminopolycarbonsäuren mit

Tabelle 1. Funktionaler Zusammenhang zwischen Inhibitorkonzentration und Restkonzentration an katalytisch wirksamen Eisen

Inhibitor	Konz. Bereich, μM	Gleichung	r	s	N
NTE	0,5–2,5	$y = -0{,}634x + 2{,}493$	−0,998	0,0033	36
ÄDTE	0,25–2,5	$y = -1{,}004x + 2{,}511$	−0,999	0,0455	72
DCTE	0,25–2,5	$y = -1{,}025x + 2{,}541$	−0,999	0,0434	72
DTPE	0,25–2,5	$y = -1{,}025x + 2{,}505$	−0,999	0,0427	72
TTAHE	0,25–2,5	$y = -0{,}993x + 2{,}512$	−0,999	0,0498	62
TTHE	0,20–1,2	$y = -1{,}715x + 2{,}516$	−0,998	0,0477	44

y = Konzentration an katalytisch wirksamen Eisen, μM.
x = Konzentration an Ligand in der Probe, μM.
s = Gesamtstandardabweichung von y, μM.
r = Korrelationskoeffizient.
N = Zahl der Bestimmungen.

ausgeprägtem Komplexbildungsvermögen ($K_{M \cdot L} \geq 2 \cdot 10^{10}$) sehr empfindlich, aber in bezug auf die einzelnen Liganden unspezifisch. Bei einem Gemisch ist deshalb nur eine summarische Bestimmung möglich. Allerdings liegen in der Praxis selten Gemische von Sequestrierungsmitteln vor, da meist gezielt nur ein bestimmter Komplexbildner eingesetzt wird, der dann mit den o.g. Einschränkungen bestimmt werden kann. Ausgehend von der guten Linearität zwischen Meßgröße (Extinktion) und Inhibitorkonzentration konnten empfindliche mechanisierte Bestimmungsverfahren für einige α-Aminopolycarbonsäuren ausgearbeitet werden. Ausführlich wurde eine ÄDTE-Bestimmung in natürlichen (auch eisenreichen) Wässern getestet, über die an anderer Stelle[24] berichtet wird.

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Summary—α-Aminopolycarbonic acids and condensed phosphates are inhibitors in the iron-catalysed oxidation of *p*-phenetidine with hydrogen peroxide. By means of a flow-through system the inhibiting properties of seven α-aminopolycarbonic acids and technically important phosphates were investigated and the results are explained in terms of complex formation by the inhibitors. An automated determination is possible for some α-aminopolycarbonic acids (tetra-, penta- and hexa-acids) in a concentration range from 2.5×10^{-7} to $2.5 \times 10^{-6} M$ with good reproducibility (relative standard deviation about ±2% in the middle concentration range).

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SOLVENT EXTRACTION OF SCANDIUM FROM MALONIC ACID WITH HIGH MOLECULAR-WEIGHT AMINES

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Summary—Scandium is quantitatively extracted with 4% Amberlite LA-1 or Amberlite LA-2 in xylene at pH 2.5–5.5 from 0.1*M* malonic acid. Scandium is stripped from the organic phase with 0.5*M* hydrochloric acid and determined spectrophotometrically at 525 nm, as its complex with Alizarin Red S. Primene JM-T, tri-iso-octylamine, tributylamine and tribenzylamine have also been studied as extractants, but found to be unsatisfactory for various reasons. Xylene, toluene, benzene, chloroform, carbon tetrachloride, hexane, cyclohexane and kerosene have been studied as diluents. Xylene is found to be the most efficient. Scandium can be separated from most metals by selective extraction, and from gallium, thallium(III), bismuth, antimony(III), chromium(III), copper(II), iron(III), uranium(VI), cerium, zirconium, indium, thorium and titanium by selective stripping, in some cases combined with use of suitable complexing media to retain the other metals in the organic phase.

dium has been separated by extraction into sol-
g solvents, or by anion-exchange chroma-
ıphy in various acid media, but few liquid anion-
ıngers have been used. It can be separated from
ıanides with a 10% solution of Amberlite LA-2
ylene, from 0.1*M* sulphuric acid containing
onium sulphate, but iron, zirconium and vana-
ı interfere strongly.[1] The separation of scan-
ı from thorium, uranium and zirconium in sul-
ɜ media has also been attempted with Amberlite
'.[2] It has been observed that extraction of scan-
ı is best with primary amines.[3] Scandium has also
extracted with ethyl tri-iododecyl ammonium
ıide in xylene in the presence of Xylenol Orange.[4]
ɜ of these methods are selective and many anions
as phosphate, chloride and nitrate interfere. Sys-
tic studies with liquid anion-exchangers in
nic acid media are almost completely lacking.
paper presents a method for the solvent extrac-
of scandium and its separation from thorium,
ınium, uranium, yttrium, lanthanides and many
r elements which are associated with it in
ɜrals.

EXPERIMENTAL

ents

ɔck scandium solution was prepared by dissolving
g of scandium oxide in 80 ml of conc. nitric acid
ɔiling until a clear solution was obtained, and diluting
itre with demineralized water. The solution was stan-
zed by EDTA titration with Xylenol Orange as indi-
.[5] It was further diluted as required.
ıberlite LA-1 [*N*-dodecyl(trialkylmethyl)amine],
ɜrlite LA-2 [*N*-lauryl(trialkylmethyl)amine]. Primene
[mixture of primary amines in the C_{18}–C_{22} range],
ɔutylamine, tri-iso-octylamine and tribenzylamine
dissolved in suitable diluents. The liquid anion-
ıngers were converted into the malonate form as de-
ɜd earlier.[6]

Buffer (pH 3.5) was prepared by dissolving 10.423 g of potassium hydrogen phthalate in 250 ml of water, adding 78.5 ml of 0.1*M* hydrochloric acid and diluting to 1 litre with demineralized water.

General procedure

A portion of solution containing 45 μg of scandium was mixed with 5 ml of 0.1*M* malonic acid, the pH was adjusted to 3.0 with 0.01*M* sodium hydroxide or malonic acid, and the volume made up to 10 ml. The solution was transferred into a separating funnel and shaken with 10 ml of 4% Amberlite LA-1 solution in xylene for 5 min (wrist-action shaker). The aqueous phase was discarded and the organic phase equilibrated with 10 ml of 0.5*M* hydrochloric acid to strip scandium. The aqueous layer was withdrawn, evaporated almost to dryness and treated with 5 ml of water. Five ml of buffer solution (pH 3.5) were added, followed by 2 ml of 0.1% Alizarin Red solution. The volume was made up to 25 ml with demineralized water and the absorbance measured at 525 nm against a reagent blank. The amount of scandium was computed from the calibration curve.[7]

RESULTS AND DISCUSSION

Extraction as a function of pH

The pH for quantitative extraction was ascertained by extracting scandium with 4% solutions of the various liquid anion-exchangers used, at pH-values in the range 1.0–7.0 (Fig. 1). The optimum pH for use of Amberlite LA-1 or LA-2 was 2.5–5.5. Extraction was not quantitative with tri-iso-octylamine, tributylamine and tribenzylamine. With Primene JM-T, although the extraction was quantitative, emulsification caused serious difficulty. Amberlite LA-1 was selected for further study.

Effect of various diluents

Solutions (4%) of Amberlite LA-1 in various diluents were used (Table 1). The phase-volume ratio was kept at 1, as otherwise an emulsion was formed. Xylene

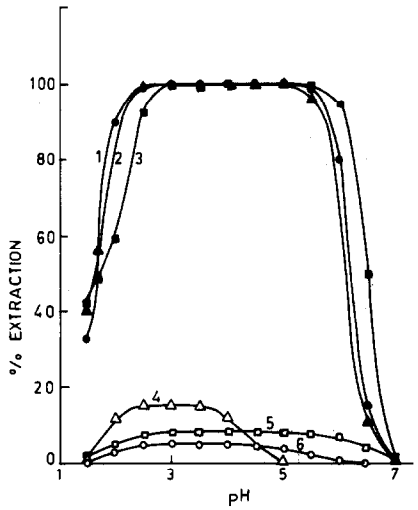

Fig. 1. Extraction of Sc from malonic acid solution by various 4% amine solutions in xylene. 1, Amberlite LA-1; 2, Amberlite LA-2; 3, Primene JM-T; 4, tri-iso-octylamine; 5, tributylamine; 6, tribenzylamine.

was found to be the most effective diluent. Benzene, toluene, chloroform or carbon tetrachloride caused either turbidity or emulsion formation. Hexane, cyclohexane and kerosene proved to be poor diluents. Extraction was found to be complete in 2 min, and a 5-min shaking period is recommended.

Reagent concentrations

Table 2 shows that extraction with 4% Amberlite LA-1 in xylene starts when the malonic acid concentration is $1 \times 10^{-3}M$ and is quantitative from $7 \times 10^{-3}M$ malonic acid. For all practical purposes, $0.1M$ concentration is recommended.

The optimum concentration of Amberlite LA-1 is >3% (Table 3), and a 4% solution is recommended.

Stripping agents

The stripping agents tested were sodium hydroxide (0.01–2.5M) ammonia (0.1–5M), hydrochloric acid (0.25–10M), nitric acid (1–8M) and sulphuric acid (0.25–4M), in 1:1 volume ratio to the organic phase.

Stripping was complete with 0.5–10M hydrochloric acid, 1–8M nitric acid and 0.5–4M sulphuric acid. With more dilute sulphuric acid (0.05–0.2M), recovery was incomplete, as a negatively-charged sulphate complex of scandium was formed, which was re-extracted by the exchanger. Although nitric acid gave satisfactory recovery, nitrate ions interfere strongly in the colorimetric determination of scandium.[7] Sodium hydroxide and ammonia were incapable of completely stripping the scandium from the organic phase. For all practical purposes 10 ml of 0.5M hydrochloric acid should be used for the stripping.

Table 1. Effect of various diluents. Sc(III)45μg; pH 3.0; 4% Amberlite LA-1 solution

Diluent	Dielectric constant, ϵ	Extraction, E, %
Benzene	2.28	99.0
Toluene	2.38	98.8
Xylene	2.30	100.0
Chloroform	4.80	99.5
Carbon tetrachloride	2.24	95.1
Hexane	1.89	66.0
Cyclohexane	2.05	44.5
Kerosene	(2)	66.0

Table 2. Effect of malonic acid concentration. Sc 45 μg; 4% Amberlite LA-1 in xylene

Malonic acid concentration, mM	Extraction, E, %
0.5	0.0
1.0	22.0
2.0	58.0
3.0	78.0
4.0	91.1
5.0	95.0
6.0	97.8
7.0	100.0
8.0	100.0

Species extracted

The extraction mechanism appears to be:

$$Sc(NO_3)_3 + 3\text{malonic acid} \rightarrow Sc(\text{malonate})_3^{3-} + 3HNO_3$$

$$3[(R_2NH_2)_2\text{-malonate}] + 2Sc(\text{malonate})_3^{3-} \rightarrow 2(R_2NH_2)_3Sc(\text{malonate})_3 + 3(\text{malonate})^{2-}$$

This was confirmed graphically. The slopes of plots of log D *vs.* log of the amine concentration at a fixed aqueous ligand concentration and of log D *vs.* log of ligand concentration at fixed amine concentration will give the composition of the extracted species. The slopes were 3.1 and 2.8 respectively, confirming therefore the composition of the extracted species as $(R_2NH_2)_3Sc(\text{malonate})_3$.

Effect of diverse ions

Scandium was extracted in the presence of various ions (Table 4); the tolerance limit was set as described

Table 3. Effect of Amberlite LA-1 concentration. Sc 45 μg; pH 3.0; diluent xylene

Amberlite LA-1, %	Extraction, E, %
0.5	10.0
1.0	54.5
1.5	77.5
2.0	90.3
2.5	94.4
3.0	97.75
3.5	100.0
4.0	100.0
5.0	100.0

earlier.[6] The alkali and alkaline-earth metal ions, thallium(I), iron(II), silver, arsenic(III), yttrium, tin(IV) and all lanthanides except lanthanum, cerium(III), praseodymium and neodymium are not extracted with scandium, as they do not form malonate complexes. Zinc, cadmium, nickel, copper(II), cobalt(II), chromium(III), aluminium, lead, lanthanum, praseodymium, neodymium, thallium(III) and manganese(II) form very weak complexes, and hence are very easily washed into the aqueous phase with water before scandium is stripped.

Gallium, bismuth, antimony(III), iron(III) and uranium(VI) form complexes with malonic acid and are therefore extracted along with scandium. However, scandium does not form a strong complex with hydrochloric acid, so it is stripped with hydrochloric acid, the chloro-complexes of the other metals being re-extracted by the exchanger.[8] They can be stripped with 1*M* sodium hydroxide.

Table 4. Effect of diverse ions. Sc 45 μg; 4% Amberlite in xylene; pH 2.5

Foreign ion	Added as	Tolerance limit, *mg*
Ag^+	$AgNO_3$	0.50
Tl^+	Tl_2SO_4	0.51
Tl^{3+}	$TlCl_3$	0.22
In^{3+}	$In_2(SO_4)_3.5H_2O$	0.13
Ga^{3+}	$GaCl_3$	0.11
Cu^{2+}	$CuSO_4.5H_2O$	0.99
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	0.51
As^{3+}	$AsCl_3$	0.28
Sb^{3+}	$SbCl_3.3H_2O$	0.19
Bi^{3+}	$Bi(NO_3)_3.5H_2O$	0.25
Pt^{4+}	$H_2PtCl_6.xH_2O$	0.28
Fe^{2+}	$FeSO_4.7H_2O$	0.48
Fe^{3+}	$Fe_2(SO_4)_3.7H_2O$	0.20
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	0.22
Al^{3+}	$Al(NO_3)_3.9H_2O$	0.50
Ti^{4+}	$Ti(SO_4)_2$	0.05
Sn^{4+}	$SnCl_4$	0.45
Th^{4+}	$Th(NO_3)_4.4H_2O$	0.05
Zr^{4+}	$Zr(NO_3)_4.5H_2O$	0.10
U^{6+}	$UO_2(NO_3)_2.6H_2O$	0.11
Y^{3+}	$Y(NO_3)_3$	0.50
La^{3+}	La_2O_3	0.23
Ce^{3+}	$Ce(NO_3)_3$	0.16
Nd^{3+}	Nd_2O_3	0.19
Pr^{3+}	Pr_6O_{11}	0.20
Sm^{3+}	Sm_2O_3	0.20
Gd^{3+}	Gd_2O_3	0.21
Dy^{3+}	Dy_2O_3	0.20
Be^{2+}	$Be(NO_3)_2.3H_2O$	0.51
Mn^{2+}	$MnSO_4.7H_2O$	0.25
Co^{2+}	$Co(NO_3)_2.6H_2O$	0.50
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	0.52
Mg^{2+}	$MgSO_4.7H_2O$	1.00
Ca^{2+}	$Ca(NO_3)_2$	1.00
Sr^{2+}	$Sr(NO_3)_2.2H_2O$	1.00
Ba^{2+}	$Ba(NO_3)_2.4H_2O$	0.41
Li^+	$Li_2SO_4.H_2O$	4.5
Na^+	NaCl	5.0
K^+	KCl	5.0
Rb^+	RbCl	1.0
Cs^+	CsCl	1.1
SeO_3^{2-}	Na_2SeO_3	0.20
TeO_3^{2-}	Na_2TeO_3	0.20
WO_4^{2-}	Na_2WO_4	0.20
$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}.4H_2O$	0.11
CN^-	KCN	0.20

Scandium can be separated from cerium and zirconium in sulphate media, and from indium and thorium in nitrate media. Cerium is first stripped with 0.05*M* sulphuric acid and then scandium with 1*M* hydrochloric acid.[8] Zirconium is separated by first stripping scandium with 0.75*M* sulphuric acid, followed by stripping of zirconium with 5*M* hydrochloric acid.[2] Indium and scandium are separated by first stripping scandium with 4*M* nitric acid, followed by stripping of indium with 1*M* hydrochloric acid. Scandium is separated from thorium by stripping it with 8*M* nitric acid, followed by stripping of thorium with 5*M* hydrochloric acid. Titanium and scandium are separated by first stripping scandium with 0.1*M* oxalic acid/0.25*M* hydrochloric acid, followed by stripping of titanium with 1*M* hydrochloric acid.[9] The interference of the nitric acid used in the stripping step is eliminated by evaporation to dryness after addition of hydrochloric acid, followed by taking up of the residue with water. Scandium is separated from anions such as selenite, tellurite, tungstate, molybdate and cyanide by selective stripping of scandium with hydrochloric acid, followed by stripping of all the oxyanions with 1*M* sodium carbonate or sodium hydroxide.

The separation of scandium from titanium, zirconium, thorium and yttrium is important as these elements are generally associated with it in minerals. The separation of uranium, silver, antimony, bismuth and selenium is important in fission product separation. From ten runs with 45 μg of scandium, the recovery was 99.8 ± 0.2%. The optimum range is 10–1200 μg of scandium. The proposed method is rapid, simple and selective.

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THE PRECONCENTRATION OF MERCURY AND METHYLMERCURY ON DITHIZONE-COATED POLYSTYRENE BEADS

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Summary—The preconcentration of "inorganic" and methyl mercury cations from aqueous solution is described. The procedure involves collection of mercury on dithizone-coated macroreticular resin beads prior to analysis by cold-vapour atomic absorption spectroscopy. The beads are readily prepared before use and give rise to quantitative selective recovery of "inorganic" and methyl mercury from fresh and saline water samples.

Several different approaches have been proposed for the preconcentration of mercury from natural waters, including solvent extraction,[1] ion-exchange,[2] freeze-drying concentration[3] and co-precipitation.[4,5] In general, however, these techniques either lack specificity or require a lot of work and reagents in the preparation of samples.

Chow and Buksak[6] have reported the use of dithizone-treated polyurethane foams for the preconcentration of ionic mercury from aqueous samples. The dithizone foam is unstable and since it cannot be rapidly prepared, is difficult to use. In order to minimize decomposition of the dithizone, resin saturated with dithizone stabilized as its zinc complex has been used for the preconcentration of mercury.[7] Although the dithizone is effectively stabilized as zinc dithizonate, recovery of the mercury from materials coated with zinc dithizonate is frequently poor and subject to high levels of contamination. In this paper we describe the use of dithizone-coated macroreticular resin beads for the preconcentration of both "inorganic" and methylmercury cations from aqueous solution. The beads can be coated rapidly before use, thus overcoming the problems of instability of dithizone, and recovery of the mercury species approaches 100%.

EXPERIMENTAL

Instruments

Cold-vapour atomic-absorption spectroscopy was performed with a Varian Techtron AA175AB spectrometer with deuterium-lamp background-correction. The mercury generator was similar in design to that described by Simpson and Nickless[8] but was a single-channel device. The mercury compounds were reduced to metallic mercury with sodium borohydride, since reduction of methylmercury with stannous chloride was incomplete.

Throughout the work the 253.7 nm mercury absorption line was used, with 1 nm band-width, and the absorbance was corrected. The mercury generator was operated with nitrogen as carrier gas at a flow-rate of 300 ml/min, and the reductant was 1% (w/v) sodium borohydride in 0.1*M* sodium hydroxide.

Reagents

Unless otherwise stated, all reagents were of analytical-reagent grade. Glassware was soaked overnight in acidic sodium dichromate solution, rinsed with distilled water and oven-dried. It was then rinsed with a 1% solution of trimethylchlorosilane in petroleum ether (b.p. 40–60°) to deactivate the surface of the glass.

Stock 1000 μg/ml mercury(II) solution was prepared by dissolving mercury(II) sulphate in 50% v/v sulphuric acid. Methylmercury chloride solution (Hg 1000 μg/ml) was prepared in 1*M* hydrochloric acid. Lower concentrations were obtained by serial dilution. Macroreticular resin beads (Amberlite XAD series, Rohm and Hass Co., Philadelphia, USA) were washed with distilled water and methanol before use.

Preparation of dithizone-coated beads

Although several methods of coating the beads with dithizone have been tried, the following procedure has been found to give high-capacity beads of reproducible performance.

Five g of wet beads are swirled in 20 ml of distilled water in a conical flask whilst 10 ml of 0.005*M* dithizone solution in acetone (freshly prepared) are added. The swirling is continued for 2 min, then the beads are rinsed several times with distilled water. Excess of dithizone is readily removed by flotation. The coated beads will keep for several days if stored under water in the dark in a refrigerator.

RESULTS

Properties of dithizone-coated beads

The effect of pH on the uptake of mercury and methylmercury cations by dithizone-coated beads has been studied by batch equilibration of 2.0 g of damp coated beads with 10 ml of 20-ng/ml mercury solution for 30 min. Uptake of both mercury(II) and methylmercury was 100% over the pH range 1–10. However, at hydrochloric acid concentrations above 8*M* the uptake of mercury dropped to zero, allowing quantitative recovery of the mercury collected (Fig. 1). In order to achieve maximum selectivity of metal uptake a pH of between 1 and 2 was chosen, as within this pH range only copper, mercury, palladium and silver are expected to be taken up by the beads. Mercury is effectively eluted from the beads with 9*M* hydrochloric acid.

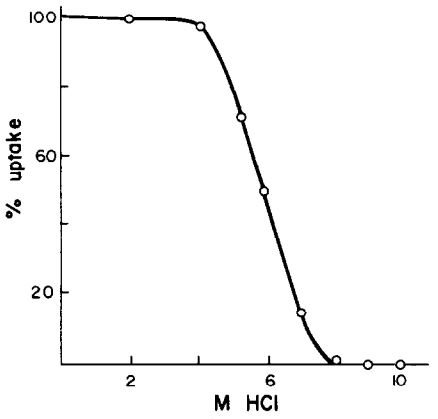

Fig. 1. Mercury uptake by dithizone-coated beads as a function of acidity.

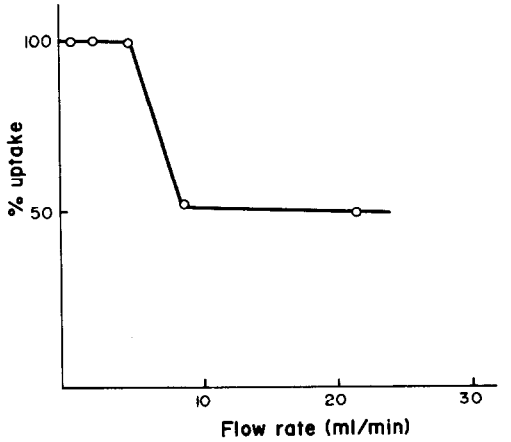

Fig. 2. Effect of flow-rate on the preconcentration of mercury from dilute solution.

A range of macroreticular resin beads was compared by batch equilibration of coated resin beads (1 g damp weight) with mercury solutions at pH 1.5 (Table 1).

The loading of the Amberlite XAD-2 beads with dithizone has been estimated by removal of the dithizone from the beads by washing with acetone, and measurement of the absorbance of the resulting solution at 612 nm. The loading was found to be 1.23 ± 0.17% w/w, on a dry weight basis, but dropped to 0.83 ± 0.22% after the beads had been washed with 9*M* hydrochloric acid.

Collection of mercury on a column of dithizone-coated beads

The effect of flow-rate on mercury uptake has been studied by passing 25-ml portions of 1-μg/ml standard mercury solution (adjusted to pH 1.5 with sulphuric acid) through 2-g (1.5-cm diameter) columns of Amberlite XAD-2 coated with dithizone. The uptake of mercury by the coated beads was assessed by analysis of the eluates (Fig. 2). In similar experiments, the rate of elution of mercury with 9*M* hydrochloric acid was varied, and 99.0 ± 1.0% recovery of mercury was found over the flow-rate range 0.5–8.3 ml/min.

To assess potential cation interferences, 50 ml of 10-ng/ml mercury(II) solution (pH 1.5) containing 20 ng of copper and silver per ml were preconcentrated on 2-g coated-bead columns. Recovery of mercury was 99 ± 1% for solutions containing both copper and silver. The presence of 0.1 g of fluoride, chloride, bromide and iodide (as their sodium salts) per 100 ml did not affect the recovery. Sulphuric acid was used for sample acidification and, at moderate concentrations, had no effect on mercury recovery. High concentrations of sodium chloride, as found in marine waters, were studied by the analysis of samples and are dealt with in a following section.

Optimum preconcentration of mercury on columns

For the optimum collection of mercury from aqueous solution, samples were acidified to pH 1–2 with sulphuric acid. The samples were then passed through 1.5-cm diameter glass columns, containing 2 g of dithizone-coated Amberlite XAD-2 resin beads, at a flow-rate of less than 5 ml/min. Mercury was eluted from the columns with 25 ml of 9*M* hydrochloric acid, at a flow-rate of approximately 5 ml/min.

Preconcentration of low-concentration mercury solutions

Unless the coated beads are washed with 9*M* hydrochloric acid before use, unacceptably high blank values are obtained. After such treatment, recovery of mercury from 1-litre standard solutions containing 50, 100 or 150 ng of mercury was found to be 97.0 ± 9.0%, with a preconcentration factor of 40. In similar experiments recovery of methylmercury was 94.2 ± 9.5%.

Table 1. Uptake of mercury(II) by 1.0 g of dithizone-coated macroreticular resin equilibrated with 10 ml of standard mercury(II) solutions

Amberlite resin	Nature	Uptake, %, from solution of concentration 1 μg/ml	10 μg/ml	100 μg/ml
XAD-1	Polystyrene	100	81.5	72.5
XAD-2	Polystyrene	100	93.0	77.5
XAD-4	Polystyrene	100	80.0	75.0
XAD-7	Acrylic ester	100	53.5	62.5
XAD-8	Acrylic ester	100	80.0	71.5

Table 2. Analysis of sea-water*

Method	Preconcentration factor	Mercury content, *ng/l*
Direct analysis without preconcentration†	—	290 ± 42
Direct analysis with preconcentration	4	328 ± 57
Standard addition before preconcentration	4	305 ± 45

* The mercury content of the sample is rather high for coastal water, but the results are intended only to demonstrate the validity of the method.
† Sample 50 ml.

The preconcentration procedure was applied to sea-water collected from a very shallow beach near a busy harbour, and filtered through a Millipore 0.45-μm pore-size membrane. The sample was analysed both directly and after preconcentration by a factor of four. Results of these analyses are given in Table 2.

DISCUSSION

Owing to the volatility of mercury, contamination from the atmosphere is a major risk during the preconcentration of mercury under normal laboratory conditions. In order to minimize such contamination, preconcentration and sample "clean-up" procedures should be designed to reduce to a minimum the contact of the sample with the atmosphere and to involve only minimal sample manipulation. Such conditions are inconsistent with preconcentration methods based on solvent extraction or co-precipitation procedures and in general column preconcentration procedures lack specificity. However, by immobilizing one of the most specific mercury-complexing agents on a solid support material it has proved possible to preconcentrate both mercury and methylmercury cations efficiently by collection on a column. In order to minimize contamination this collection is best carried out in a flow-through system either at the sampling site or in the laboratory.

Although dithizone is highly selective, thin layers and solutions of the complexing agent are relatively unstable. Macroreticular resin beads can be rapidly coated by precipitation of dithizone onto the bead surface immediately before use, thus avoiding the long soaking times required for the adsorption of dithizone onto support surfaces. It is believed that the coating is largely the result of precipitation of dithizone onto the polymer bead surface but the extent of dithizone penetration into the macroreticular matrix is not yet known. The beads coated with precipitate are rapidly and cheaply produced and are conveniently prepared before use. Once used, the beads can be either discarded or recoated.

The beads are highly selective and quantitative recovery of mercury from both fresh-water and saline samples can be achieved. Since the mercury is recovered from the beads into aqueous solution, the procedure is compatible with most assay techniques.

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SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II) WITH 2-[DI-(2-PYRIDYL)-METHYLIDENEHYDRAZINO]QUINOLINE

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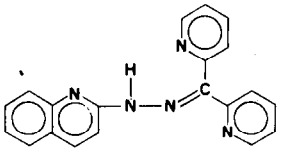
nmary—A simple, rapid and selective procedure for spectrophotometric determination of cobalt been developed. Cobalt(II) forms two water-soluble complexes with 2-[di-(2-pyridyl)methylidene-razino]quinoline, an orange-yellow complex (λ_{max} 510 nm) in the pH range 2–12 and a pink complex $_{ix}$ 530 nm) in 0.1–6*M* perchloric acid medium. The molar absorptivities for the orange–yellow pink complexes are 3.65×10^4 and 4.1×10^4 $l.mole^{-1}.cm^{-1}$ and Beer's law is obeyed up to and 2.0 ppm of cobalt(II) respectively. Cobalt(II) has also been determined in alloys.

:s, particularly hydrazones of nitrogen-con-erocyclics have attracted much attention as reagents, because of their high sensitivity vity. Lions *et al.*[1,2] first reported the ana-perties of these compounds. Their analyti-ations have recently been reviewed by *al.*[3,4] Various substituted hydrazones [for pyridine-2-aldehyde-2-quinolylhydrazone,[5] yridine-2-pyridylhydrazone,[6] benzil mono-ydrazone[7]]* have been used for the spectro-ic determination of cobalt.[8–11] In the nmunication the synthesis of 2-[di-(2-pyri-idenehydrazino]quinoline (DPMHQ) and ion in the determination of micro amounts re described.



DPMHQ

ous solution, DPMHQ reacts with Co(II) orange-yellow complex (λ_{max} 510 nm). On f perchloric acid this complex shows a mic shift from 510 to 530 nm and gives nplex that is stable even in 5*M* perchloric ium. Since all other transition metal–complexes are decomposed in 5*M* per-d medium, this property has been utilized ing a selective method for determination

t two of these names are comparatively in-ut not precise: more precise but less informa-for these two compounds are 2-(2-picolinyl-ino)quinoline and 2-[phenyl(2-pyridyl)methyl-ino]pyridine [Ed.].

EXPERIMENTAL

Reagents

DPMHQ was synthesized by refluxing equimolar quantities of di-2-pyridyl ketone with 2-hydrazinoquinoline in ethanolic medium for about 6 hr. The crude compound which separated on cooling was crystallized from ethanol to give pale yellow needles, m.p. 155°. The purity was checked by thin-layer chromatography. Elemental analysis confirmed the synthesis (found, C 73.2%; H 4.6%; N 21.8%: required, C 73.8%; H, 4.6%; N, 21.5%). DPMHQ solutions were prepared in ethanol (95%) and stored in amber glass bottles.

Standard solutions of Co(II) were prepared by dissolving pure cobalt metal in perchloric acid and standardized volumetrically.

Dilute perchloric acid and sodium hydroxide solutions were used for pH adjustments.

Solutions for interference studies were prepared by dissolving analytical reagent grade chemicals in doubly distilled water.

Procedure with orange-yellow complex

To a suitable aliquot containing 2.2–17.3 μg of cobalt(II), add 2 ml of $10^{-2}M$ ethanolic DPMHQ solution. Adjust the pH to 6. Dilute to 10 ml so that the final ethanol content is 50% v/v. Measure the absorbance at 510 nm against a reagent blank prepared under identical conditions.

Procedure with pink complex

To a suitable aliquot containing 2.2–18.5 μg of cobalt(II) add 2 ml of $10^{-2}M$ ethanolic DPMHQ solution. Adjust the acidity to 3*M* perchloric acid. Dilute to 10 ml. Measure the absorbance at 530 nm against a reagent blank prepared under identical conditions.

RESULTS AND DISCUSSION

Spectral behaviour of complexes

A pH study of the complexation of DPMHQ with Co(II) showed that the orange-yellow complex (λ_{max} 510 nm) has constant absorbance in the pH range

2–12. This complex shows a bathochromic shift to 530 nm on addition of perchloric acid. The new pink complex is stable even in 5*M* perchloric acid medium.

Effect of DPMHQ concentration and stability of the complexes

For complete complexation a 3:1 ratio of ligand to metal is sufficient in both cases. The reagent does not absorb at the wavelength of maximal absorption of either cobalt complex. This is advantageous because the excess of reagent is not critical and a blank is necessary only to check the purity of the reagents used to adjust the conditions for the reaction. Both complexes are stable for up to 24 hours.

Characteristics of the complexes

The Co(II)–DPMHQ complex is formed in the pH range 2–12 but not in highly acidic medium, because of strong protonation of the ligand. Both complexes have a ligand:metal ratio of 2:1.

Orange-yellow complex. Beer's law is obeyed up to 1.84 ppm. The optimum concentration range evaluated by Ringbom's method is 0.22–1.73 ppm. The molar absorptivity is 3.65×10^4 $1.mole^{-1}.cm^{-1}$ at 510 nm.

Pink complex. Beer's law is obeyed up to 2.0 ppm. The optimum concentration range evaluated by Ringbom's method is 0.22–1.85 ppm. The molar absorptivity is 4.1×10^4 $1.mole^{-1}.cm^{-1}$ at 530 nm.

Interferences

An error of $\pm 2\%$ in the absorbance reading was considered tolerable. The concentrations of other ions tolerable (in ppm) the determination of 0.59 ppm of cobalt are given below in parentheses for both the complexes.

Table 1. Determination of cobalt (%) in alloys (*n* determinations)

Alloy	Co reported	Co found	*n*	Relative SD %
"K" Monel wire	0.51	0.50	8	4.0
Nilo-K wire	17.4	17.7	8	1.5

Orange–yellow complex. Bromide, iodide, chloride, nitrate, phosphate, fluoride, acetate, citrate, tartrate, thiourea, thiosulphate, borate, thiocyanate (2000 ppm each); nitrite, sulphite, sulphate (1000 ppm each); oxalate (500 ppm); Ca, Sr, Ba, Mg, Pb, Ti, Sn(II), Al, Sb(III), Mo(VI), W(VI), Ag, Ni, Zn (40–60 ppm each); Cu(II), Mn(II), Fe(II), Cd and Hg(II) interfered seriously. However, Cu(II) (40 ppm); Mn(II) (40 ppm); Cd (30 ppm); Hg(II) (50 ppm) and Fe(II) (20 ppm) are tolerated if masked with thiosemicarbazide, citrate, thiocyanate, iodide and phosphate, respectively. EDTA, cyanide, persulphate and V(V) interfere seriously.

Pink complex. Bromide, iodide, chloride, fluoride, sulphite, sulphate, nitrate, thiosulphate, thiourea, citrate, borate (2000 ppm each); nitrate, acetate, phosphate, tartrate, oxalate (1000 ppm each); thiocyanate (500 ppm); Ca, Sr, Ba, Mg, Pb, (400 ppm each); Al, Sb(III), Ti (300 ppm each); Mn(II), Mo(VI), W(VI), Sn(II) (200 ppm each); Ni, Zn, Cd, Hg(II), Ag, Fe(II) (100 ppm each). Cu(II) (80 ppm) and V(V) (20 ppm) are tolerated if the perchloric acid concentration is increased from 3 to 5*M*. Serious interference is caused by EDTA, cyanide and persulphate.

Determination of cobalt in alloys

Cobalt has been determined in alloys with DPMHQ in highly acidic conditions, and the results are summarized in Table 1.

Table 2. Sensitivities of methods for the spectrophotometric determination of cobalt(II)

Method	Sensitivity, $\mu g/cm^2$*	λ, nm	Reference
Pyridine-2-aldehyde-2-quinolyl-hydrazone	0.0019	510	5
2-Benzoylpyridine-2-pyridyl hydrazone	0.0020	478	6
Benzil mono (2-pyridyl)hydrazone	0.0021	535	7
Salicylaldehydehydrazone	0.0074	450	8
o-Hydroxybenzaldehyde isonicotinolylhydrazone	0.0029	420	9
2,2'-Pyridil-2-pyridylhydrazone	0.0021	489	10
Nitroso-R-salt	0.0019	420	12
	0.0042	520	
o-Nitrosoresorcinol	0.0025	430	12
Dithio-oxamide	0.0046	430	13
Di-2-pyridyl ketoxime	0.0029	388	14
2,3-Quinoxalinedithiol	0.0016	505	15
	0.0064	598	
Phenanthrenequinonemonoxime	0.0033	420	16
DPMHQ (pH^{2-12})	0.0016	510	Present
DPMHQ (2–5*M* $HClO_4$)	0.0014	530	method

* For 0.001 absorbance.

Comparison with other reagents

DPMHQ is one of the most sensitive of the substituted hydrazones as a reagent for cobalt and compares favourably with other cobalt reagents. The method is simple, works over a wide range of acidity and is fairly free from interferences. There is no need for extraction. The reaction is instantaneous and the complexes formed are stable for a long time. Large excesses of ligand do not interfere, which is an advantage over nitrosonaphthol reagents. The sensitivities of the various methods are compared in Table 2.

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PRECONCENTRATION OF TRACES OF SILVER AND BISMUTH FROM COBALT AND NICKEL AND THEIR NITRATES, WITH ACTIVATED CARBON

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Summary—A method is described for the preconcentration of trace metals Ag and Bi, present as impurities in high-purity cobalt and nickel metals and their nitrates. After the metal samples have been dissolved in nitric acid (or the salts in water) the trace elements are complexed with ammonium pyrrolidinedithiocarbamate (APDC). The sample solution is then filtered through a 2-cm filter paper coated with 50 mg of activated carbon, whereby the complexed trace metals are adsorbed on the activated carbon and separated from the matrix. The trace elements are dissolved off with nitric acid and determined by flame atomic-absorption spectrometry (AAS). The detection limits for the analysis of 10 g of metal samples and 50 g of the nitrate samples were 0.002–0.035 ppm Ag and 0.04 ppm Bi for the metal samples, and 0.0003–0.0004 ppm Ag and 0.004–0.005 ppm Bi for the nitrate samples. The coefficient of variation, in general, is 10–25% for Ag and 33% for Bi.

Jackwerth *et al.*[1] devised a method for trace enrichment based on use of activated carbon as an adsorbent. The method depends on the specific and hydrophobic adsorption character of the activated carbon; most reagents used for the solvent extraction into organic solvents appear to be adsorbed on the activated carbon and are thus applicable with this method. With ethyl xanthate (EtX) some 10 trace metals could be quantitatively separated and enriched on the activated carbon from zinc[2] and manganese[3] matrices. However, almost none of the trace elements could be enriched when other matrices such as cobalt and nickel were used. In the present paper, ammonium pyrrolidinedithiocarbamate (APDC) is examined as the reagent for specific adsorption on activated carbon.

EXPERIMENTAL

Reagents

Cobalt and nickel powder, and guaranteed-reagent grade (G.R.) cobalt(II) and nickel(II) nitrates were used as the test samples. Activated carbon (G.R.), ammonium pyrrolidinedithiocarbamate (G.R.) and nitric acid of super special grade (S.S.G., Wako Pure Chemical Industries Ltd.) were used without further purification. Standard solutions were the same as described previously.[2] The water used was prepared by distilling demineralized water from dilute alkali and permanganate in a glass still.

Preparation of sample solutions

$Co(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ (50.00 g) was weighed out and dissolved in 300 ml of water, and 5 ml of 0.01 mg/ml APDC solution were added. The pH was 3.5–4.3. Cobalt or nickel powder (10.00 g) was weighed into a 100-ml beaker and dissolved by adding slowly 45 ml of concentrated nitric acid for cobalt or 50 ml for nickel. The solution was heated on a hot-plate at about 200° for 8–12 hr to remove excess of nitric acid, and then transferred to a 300-ml beaker with water. When the solution became turbid because of hydrolysis a little nitric acid was added to give a final pH of 3.5–4.5 in a total volume of

Table 1. Dependence of trace recovery on pH and the amount of APDC*

	Recovery %			
	Ag		Bi	
(0.05 mg of APDC)	I	II	I	II
pH				
0	30	34	31	23
1	86	85	88	86
2	89	94	87	67
2.5	91	95	88	76
3.0	83	95	89	77
3.5	93	96	90	82
4.0	100	100	90	90
4.5	94	96	85	85
APDC, *mg* (pH 3.5–4.5)				
0	0	8	68	71
0.001	32	26	68	80
0.01	89	100	85	71
0.02	100	100	87	90
0.05	100	100	89	91
0.10	100	100	89	72
0.25	96	90	68	92

* Calibration ranges of trace elements were 0.4–2.0 μg for Ag and 4–20 μg for Bi.
I—Matrix 50 g of $Co(NO_3)_2 \cdot 6H_2O$.
II—Matrix 50 g of $Ni(NO_3)_2 \cdot 6H_2O$.

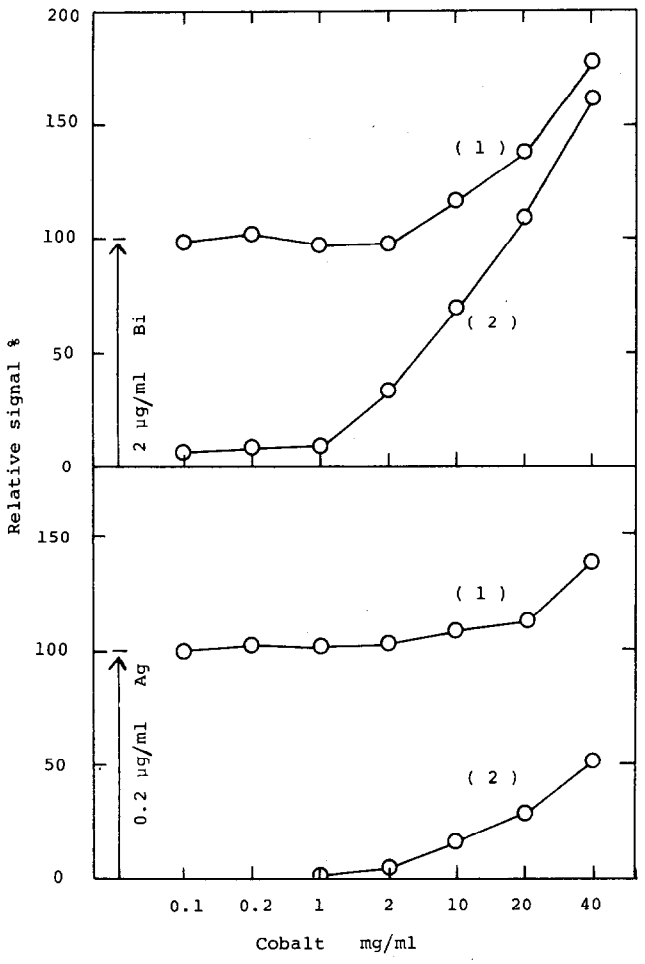

Fig. 1. Dependence of the AAS signal height of Ag (0.2 µg/ml) and Bi (2 µg/ml) on the concentration of cobalt.

300 ml and 5 ml of 0.01 mg/ml APDC solution were then added.

Procedure

The 300 ml of sample solution containing the given amount of APDC were filtered through a 2-cm diameter filter paper coated with 50 mg of activated carbon. The filter paper was dried at 60° for 30 min and the activated carbon was treated with 1 ml of hot nitric acid and the solution evaporated to dryness. Then 2 ml of 20% nitric acid were added and the carbon was removed by filtration. The concentrations of the trace metals in the solution were measured by the injection method[4,5] on 100-µl subsamples with a Hitachi 518 Atomic Absorption Spectrometer.

Blank experiments

Separate 50-ml portions of the concentrated nitric acid (S.S.G.) were heated on a hot-plate at about 200° for 7–17 hr at the same place in the fume-cupboard as that used for dissolution of the metal samples. No appreciable amount of Ag and Bi could be detected, so blank corrections for the dissolution procedures were not necessary.

Table 2. Determination of trace metals Ag and Bi in cobalt and nickel metals and nitrates*

Sample	Trace metal	Content, *ppm*	Recovery, %	C.V. (N = 10),† %	Limit of detection, 3σ (N = 24),‡ *ppm*	Matrix adsorbed, *mg*
Co (10.00 g)	Ag	0.009	95–100	23	0.002	0.09–0.21
	Bi	0.06	80–90	32	0.04	
Ni (10.00 g)	Ag	0.045	95–100	24	0.0035	0.17–0.26
	Bi	—	80–90	—	0.04	
$Co(NO_3)_2 \cdot 6H_2O$	Ag	0.004	95–100	19	0.0003	0.10–0.20
(50.00 g)	Bi	0.007	80–90	33	0.005	
$Ni(NO_3)_2 \cdot 6H_2O$	Ag	0.002	95–100	12	0.0004	0.14–0.18
(50.00 g)	Bi	0.007	80–90	33	0.004	

* Measurements of trace metals were made with a Hitachi 518 AAS with a C_2H_2–air flame.
† C.V. = Coefficient of variation, N = number of replicates.
‡ σ = Standard deviation.

RESULTS AND DISCUSSION

It was found that silver and bismuth could be separated from a cobalt or nickel matrix by using APDC as auxiliary agent in adsorption of the trace elements although traces of metals such as Cu, Cd, Fe, Mn, Pb, Tl, and Zn could not. It is suggested that this selectivity may be due to cobalt or nickel being able to displace Cu *etc.* from their APDC complexes, but not Ag or Bi. The recovery strongly depends on the working conditions. Table 1 shows the pH-dependence of trace recovery for preconcentration from 50 g of $Co(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$; the optimum working range would be pH 3.5–4.5. Table 1 also gives the dependence of recovery on the amount of APDC added. At least 0.02 mg of APDC will be needed for a cobalt matrix and 0.05 mg for a nickel matrix. Therefore, in the subsequent experiments 0.05 mg of APDC and pH 3.5–4.5 were used as working conditions. When 300 ml of solution at pH 3.5–4.5 and containing 0.05 mg of APDC and 10 g of cobalt or nickel, or 50 g of $Co(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ were filtered through a filter paper coated with 50 mg of activated carbon, Ag and Bi were retained with 95–100 and 80–90% completeness, respectively. For the calibration ranges of 0.4–2.0 μg of Ag and 4–20 μg of Bi per 10 g of metal or 50 g of metal nitrate, plots of amount of Ag and Bi recovered against amount added were linear with slopes of 0.95–1.0 for Ag and 0.8–0.9 for Bi, but with intercepts on the recovery axis, arising (presumably) from impurities in the activated carbon, and representing analytical blanks which must be subtracted from the values obtained. These blank values were 0.075 μg for Ag and below the limit of detection for Bi. The sample solutions were treated as described above and the amounts of trace metals separated from the matrix were determined by flame AAS. The results obtained are listed in Table 2.

In flame AAS, a high background of non-atomic absorption with a simultaneous and considerable decrease in trace-metal signal occurs because of the high salt content of the sample solution. This leads to poor sensitivity and detectability for the trace elements. Figure 1 shows the influence of cobalt on the AAS signals for Ag and Bi; curve 1 represents the signal heights given by solutions of increasing cobalt content and containing a constant amount of Ag (0.2 μg/ml) or Bi (2 μg/ml). The absorption values of the "non-atomic" part of the absorption signals, measured with a deuterium-lamp, are shown in curve 2. The net signal is the difference between the values on curves 1 and 2. The background signal (curve 2) begins to increase steeply at a cobalt concentration of more than 2 mg/ml for the silver signal and 1 mg/ml for the bismuth signal. Nickel gave similar behaviour. Therefore, if small amounts of silver and bismuth have to be determined in samples of cobalt and nickel, it is necessary to separate the trace elements from the matrix as completely as possible. In the present study the amount of matrix metal adsorbed on the activated carbon together with the trace metals was 0.1–0.2 mg of cobalt and 0.14–0.26 mg of nickel, which in the final 2 ml of solution is insufficient to affect the trace-metal signals.

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PRECIPITATION OF URANIUM FROM LOW-LEVEL LIQUID WASTES

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Summary—A method for the recovery of uranium from low-level liquid wastes is described. Uranium(VI) is reduced to uranium(IV) in sulphuric–phosphoric acid solution with iron(II). The uranium(IV) is precipitated as the double fluoride with sodium. The uranium content of the filtrate is in the low ppm range. Possible modifications to the procedure are discussed.

ge amounts of liquid waste are generated by our ana- cal laboratory support of high enriched uranium oper- ons. The uranium concentration of process materials is ermined by titration with standard potassium dichro- te after reduction by one of several possible methods. e reducing agents used are iron(II), amalgamated zinc nes reductor) and chromium(II). Iron(II) is used in fairly ncentrated phosphoric acid medium, but the reductions h the Jones reductor and chromium(II) are accom- hed in dilute sulphuric acid. The average waste from se analyses is strongly acidic with sulphuric acid and ntains large amounts of phosphoric acid. About one gram of highly enriched uranium is contained in the oratory waste accumulated in a month.

The high value of the uranium makes recovery very active. However, attempts to recover the uranium by extraction system used routinely in the facility produce nerous problems. In the extraction process, the aqueous vent used is 3–5*M* nitric acid containing some hydro- ric acid. Aluminium nitrate is added to complex the oride. The uranium is extracted with a 30% solution of utyl phosphate in a refined kerosene. Bleeding the te into aqueous solvent even at a volume ratio as low 1:40 caused the residual uranium level in the aqueous se after extraction to be too high for discharge into plant waste system. This was attributed to the high sphate and sulphate level of the laboratory waste. As sult, the rate of addition of waste that could be toler- d was so low that the processing rate was only about the generation rate and a significant stockpile was eloping. Without a suitable recovery method, the nium would have to be fixed in cement and placed drums for burial, a time-consuming and expensive cess.

High enriched operations preferred not to alter the action process to accommodate the waste. A search an for alternative methods to isolate the uranium from sulphate–phosphate matrix prior to extraction. The hods studied included precipitation with sodium or assium hydroxide, partial neutralization with alkali owed by precipitation with 8-hydroxyquinoline, and aration on ion-exchange resins. The methods had some cess but were time-consuming and inefficient for nium recovery.

Uranium(IV) is precipitated as the insoluble fluoride from acid solution. The double fluorides of uranium with ammonium, sodium and potassium are even more insoluble.[1] Uranium can be reduced to the quadrivalent state by the commonly used reducing agents and also by iron(II) after the addition of excess of hydrofluoric acid.[2] In the present work, the uranium is precipitated from the laboratory waste as the double fluoride with sodium.

EXPERIMENTAL

Apparatus

An Orion Model 801 digital mV/pH meter equipped with platinum and calomel electrodes was used for potential measurements in the uranium titration. The waste liquids were collected in 11-litre polyethylene bottles. A peristaltic pump was used to move the sample through a 8-in. Büchner funnel containing a medium fast filter paper. Trace uranium solutions were spotted on Schleicher and Schüll No. 211Y confined-spot test-paper and analysed with a Philips Electronics Model XRG 3000 X-ray spectrometer.

Reagents

Chemicals used for the analytical determination of uranium were reagent grade. Solutions were prepared according to ASTM method C-696.[3] All other reagents were technical grade or better. National Bureau of Standards SRM 950a uranium oxide or SRM 960 uranium metal was used to prepare standard uranium solutions.

Procedure

The laboratory waste is collected in 11-litre polyethylene bottles. Each bottle must have about one litre of headspace to allow for addition of chemicals. The uranium level is determined by ASTM method C-696.[3] To precipitate the uranium, 750 g of sodium hydroxide flake are added slowly, in 10–20-g portions, with stirring. One gram of iron metal powder is then added for each gram of uranium calculated to be present in the solution. A minimum of 30 g should be added. After the iron has dissolved, about 450 g of concentrated hydrofluoric acid are added slowly and the mixture is left to stand for 3 hr (or, preferably,

overnight). The solution is then pumped through a medium fast paper on a Büchner funnel. The green precipitate is dissolved in nitric acid and extracted with 15% tributyl phosphate solution in kerosene to recover the uranium. A small portion of the filtrate is dried on spot-test paper. The uranium $L_{\alpha 1}$ radiation is measured by X-ray emission and compared with that of standards prepared in the same manner.

RESULTS AND DISCUSSION

Preliminary investigations indicated that the phosphoric acid level had little effect on the precipitation. The amount of free sulphuric acid must be controlled since precipitation is not complete at high acidities. Addition of sodium hydroxide serves to neutralize a portion of the acid and provide a source of sodium. Iron metal powder is a convenient source of iron(II). Iron(II) salts are also effective. In the presence of excess phosphoric acid or hydrofluoric acid, the UO_2^{2+}/U^{4+} and Fe^{3+}/Fe^{2+} potentials are displaced in opposite directions. The uranium is easily reduced. The effect is due to precipitation of the uranium(IV) fluoride and/or complexation of iron(III). Typical results are shown in Table 1. The uranium measurements are the average values for two or more batches of laboratory waste.

Recoveries are excellent, typically above 99.5%. There is no clear relationship between the amount of uranium present in the solution originally and the amount found in the filtrate. Higher filtrate values observed in some cases may have been due to leakage around the filter paper.

Several variations of the proposed process exist. If the sulphuric acid level is $<1N$, addition of sodium hydroxide is not necessary; a sodium source, such as sodium sulphate, can be used to give the more insoluble double fluoride with sodium. Alternatively, in dilute sulphuric acid medium, alkali metal fluorides or ammonium fluoride could be used to form the respective double fluoride compounds with uranium. Pu(IV) also forms an insoluble double fluoride with sodium and potassium.[4] Slight modifications to the method should allow for recovery of plutonium from acid waste solutions.

Table 1. Fluoride precipitation of uranium

Waste volume, *l.*	Initial uranium, *g/l.*	Final uranium, *mg/l.*
20	2.0	4
20	1.5	3
20	2.0	2
20	1.8	<2
20	1.6	<2
20	2.8	<2
20	2.8	4
20	2.3	3
20	2.6	<2
20	4.8	<2
20	1.5	<2
20	2.4	2
20	2.7	<2
200	1.5	7
200	4.7	10

The proposed process is shown to be very effective for the removal of uranium from waste solutions containing sulphuric and phosphoric acids. The waste volume is increased by only about 10%. Usually, the uranium level of the waste filtrate is low enough for it to be diluted with the rest of the plant discharge and dumped. The amount of fluoride in the filtrate is nearly equal to the amount added, and is removed by treatment with lime before discharge of the filtrate.

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DETERMINATION OF MERCAPTOPYRIMIDINES WITH COPPER(II) IN ACETONITRILE

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Summary—A non-aqueous oxidimetric method is described for the determination of mercaptopyrimidines with copper(II) perchlorate in acetonitrile, diphenylamine being used as indicator. A bright platinum wire is used as indicator electrode and a modified calomel or an antimony electrode as reference for potentiometric titrations. The method, based on the oxidation of the mercapto group to the disulphide, is simple, accurate and reliable.

The instability of copper(I) in aqueous solution and its susceptibility to aerial oxidation have been the main difficulties in aqueous redox titrations involving copper(II) as an oxidant. The use of an acetonitrile solution of copper(II) as a redox reagent has the advantage that the resulting copper(I) is stabilized by solvation[1] and is resistant to aerial oxidation. Because of the stabilization of copper(I) relative to copper(II), the potential of the copper(II)–(I) couple is increased markedly. The formal reduction potential for the couple is 0.798 V *vs.* a silver/0.01*M* silver nitrate reference electrode.[2] This is higher than the potential of the hexanitratocerium(IV)–(III) couple, 0.755 V, in this solvent.

Acetonitrile solution of copper(II) has been described as a powerful oxidant having the ability to oxidize several compounds quantitatively.[3–8] Verma and Kumar[9,10] have recently employed copper(II) in acetonitrile for the determination of xanthates, organotrithiocarbonates and ascorbic acid. The determination of heterocyclic thiols is of importance since the compounds find application as vulcanization accelerators and have bactericidal activity. The present communication reports the non-aqueous oxidimetric determination of mercaptopyrimidines with hydrated copper(II) perchlorate in acetonitrile solution. The determinations are based on the oxidation of the thiol group to the disulphide.

$$2\text{–SH} + 2\text{Cu(II)} \rightarrow \text{–S–S–} + 2\text{Cu(I)} + 2\text{H}^+$$

EXPERIMENTAL

Apparatus

Potentiometric titrations were performed with a Toshniwal-CL06A potentiometer, with a bright platinum wire as indicator electrode and a modified calomel (saturated methanolic potassium chloride solution instead of aqueous) or antimony electrode as reference.

Reagents

Acetonitrile. Distilled twice from phosphorus pentoxide (5 g/l.).

Hydrated copper(II) perchlorate, 0.02M, in acetonitrile. Prepared and standardized as described earlier.[10]

Mercaptopyrimidines. Prepared by the method of Mathes[11] and purified by repeated crystallization until their melting points corresponded to those of analytically pure samples.

Indicator solution. A 0.10% diphenylamine solution in acetonitrile.

Procedure

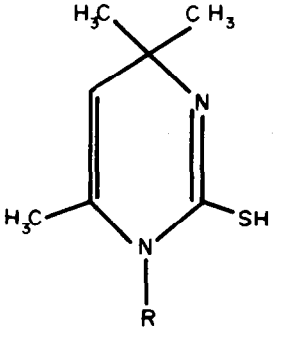
Portions of solutions of each mercaptopyrimidine in acetonitrile were transferred to dry titration vessels and diluted with 25–30 ml of acetonitrile. For visual titrations, 2 or 3 drops of the indicator solution were added and the solution was titrated at room temperature (25°) with the copper(II) perchlorate solution in acetonitrile from a microburette provided with a guard tube containing silica gel to protect the titrant from atmospheric moisture. The end-point was marked by the appearance of a violet or deep blue colour. The solution was mechanically stirred (magnetic stirrer) during the potentiometric titration and a sharp jump in potential was observed at the equivalence point, with either reference electrode.

RESULTS AND DISCUSSION

The results recorded in Table 1 indicate that mercaptopyrimidines can be determined by titration with copper(II) in acetonitrile. The results obtained potentiometrically were the same for both types of reference electrode, so only those for the calomel electrode are recorded. In potentiometric titrations the potentials became stable immediately after each addition of the oxidant. A sharp jump in potential of 210–380 mV (antimony reference electrode) or 200–400 mV (modified calomel reference electrode) for 0.05 ml of 0.02*M* copper(II) perchlorate was observed at the equivalence point. The potentials at the inflection points were 180–260 mV (antimony electrode) and 200–320

Table 1. Titration of mercaptopyrimidines with hydrated copper(II) perchlorate in acetonitrile

Mercapto-pyrimidine*	Amount found†§ mg		Amount found§‡ mg	
	Visual method	Potentiometric method	Visual method	Potentiometric method
mpA	4.02, 0.038	4.01, 0.031	16.08, 0.043	16.03, 0.041
mpB	4.03, 0.029	3.99, 0.021	15.91, 0.056	16.05, 0.055
mpC	3.97, 0.031	3.99, 0.030	15.93, 0.061	16.05, 0.047
mpD	4.00, 0.037	3.98, 0.029	16.11, 0.043	15.90, 0.045
mpE	3.97, 0.028	3.97, 0.022	16.08, 0.053	15.91, 0.049
mpF	4.02, 0.032	3.99, 0.021	16.06, 0.039	15.89, 0.040
mpG	3.97, 0.032	3.99, 0.028	16.00, 0.053	16.10, 0.030
mpH	4.01, 0.028	4.00, 0.027	15.88, 0.046	15.91, 0.029
mpI	4.03, 0.036	4.02, 0.022	16.11, 0.057	15.99, 0.040



mpA, R = methyl
mpB, R = n-butyl
mpC, R = n-pentyl
mpD, R = phenyl
mpE, R = *o*-tolyl
mpF, R = *p*-tolyl
mpG, R = *o*-methoxyphenyl
mpH, R = *p*-methoxyphenyl
mpI, R = naphthyl

† Amount taken, 4 mg.
§ Figures quoted are the averages of ten determinations, together with the standard deviations.
‡ Amount taken, 16 mg.

mV (calomel electrode). The overall standard deviations calculated from the pooled data (performed with 4-mg samples of each mercaptopyrimidine) were 0.032 and 0.026 mg for the visual and potentiometric titrations respectively. When 16 mg of each mercaptopyrimidine were used, the corresponding values were 0.050 and 0.042 mg respectively.

The oxidation of mercaptopyrimidine appears to proceed in two stages.

$$4\text{–SH} + 2\text{Cu(II)} = \text{–S–S–} + 2\text{–SCu} + 2\text{H}^+$$

(from the mercaptopyrimidine)

$$2\text{–SCu} + 2\text{Cu(II)} + 16\text{CH}_3\text{CN} = \text{–S–S–} + 4[\text{Cu(CH}_3\text{CN)}_4]^+$$

The resulting copper(I) is stabilized by the formation of a complex, $[\text{Cu(CH}_3\text{CN)}_4]^+$, with acetonitrile. The formation of this complex has been established by Morgan.[12] The appearance of brown precipitates (due to the formation of cuprous sulphide) and their dissolution (oxidation to disulphide) may be observed in the titrations.

No interferences were observed from glucose, fructose, maltose, organo-isothiocyanates, isocyanates or carbon disulphide up to 5 times the amount of the mercaptopyrimidines. Amines, mercaptans, thioureas, xanthates and dithiocarbamates interfere.

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ANALYTICAL DATA

CONDENSATION OF SOME SUBSTITUTED SALICYLALDEHYDES WITH HYDRAZINE

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Summary—Hydrazones and azines of 5-chloro-, 5-bromo-, 3,5-di-iodo-, 5-nitro- and 3-nitro- salicylaldehydes have been prepared by condensation with hydrazine. They have been characterized by their melting points, solubilities, elemental analysis and infrared spectra. Ambiguous literature on some of the compounds has also been clarified. Conditions for smooth condensation have been worked out. The extent of the condensation is found to depend on the nature of the substituent group in the salicylaldehydes.

Hydrazones in general are prepared by refluxing the stoichiometric amounts of the appropriate hydrazine and aldehyde (or ketone) dissolved in a suitable solvent. The reaction with substituted (phenyl-, *p*-nitrophenyl- and 2,4-dinitrophenyl-) hydrazines is extensively used in detection, determination and isolation of carbonyl compounds. Some substituted hydrazones[1,2] have been used in analysis and in the study of human and plant physiology but as we pointed out earlier,[3] the condensation of aromatic aldehydes with hydrazine to prepare hydrazones is difficult because of formation of the more stable azines, which is the main reason for the meagre and ambiguous literature on the hydrazones and azines. Though some of the azines[4–8] have been prepared and studied, very little work has been done on hydrazones.[8–11]

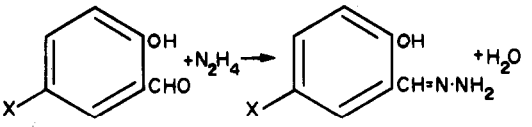
In the present study some substituted salicylaldehydes were prepared and condensed with hydrazine to yield the corresponding hydrazones or azines. Some compounds hitherto not mentioned in the literature have been isolated and characterized. An attempt has also been made to resolve the ambiguities in the literature on some of the known condensation products.

EXPERIMENTAL

5-Chloro-, 5-bromo-, 3,5-di-iodo-, 5-nitro- and 3-nitro-salicylaldehyde were prepared by standard methods.[12–14]

Formation of hydrazones

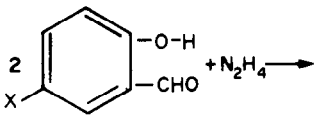
These were prepared by slowly adding 0.1 mole of substituted salicylaldehyde (dissolved in alcohol) to 0.1 mole of hydrazine hydrate in 50 ml of alcohol. A slight excess of hydrazine hydrate was used to avoid the formation of azine. The mixture was shaken thoroughly after each addition, refluxed for an hour on a water-bath and cooled; the hydrazone then separated. The products were recrystallized from methyl alcohol as crystalline needles.

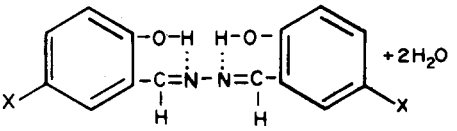


X is the substituent group in the salicylaldehyde.

Formation of azines

These were prepared by slowly adding 0.1 mole of hydrazine hydrate to 0.2 mole of substituted salicylaldehyde dissolved in alcohol, refluxing on a water-bath for half an hour and then cooling. The product was filtered off and washed with alcohol. The salicylaldazines were obtained (as powders) in good yields.





All the azines are practically insoluble in common polar organic solvents, sparingly soluble in non-polar organic solvents and aqueous ammonia but soluble in alkalis.

The identity of the compounds was established by elemental analysis and infrared spectroscopy. The hydrazones and azines were distinguished by the difference in their melting points and solubilities. Their characteristics are summarized in Table 1.

RESULTS AND DISCUSSION

The reaction of aliphatic aldehydes with hydrazine is so rapid that the hydrazones formed as intermediate products cannot be isolated, and even in

Table 1. Characteristics of substituted salicylaldehyde hydrazones and azines

Substituent	*Hydrazones m.p., °C	Colour	Solubility	Azines m.p., °C	Colour
5-chloro	84	white	A	288	yellow
5-bromo	80	white	A	305	yellow
5-nitro	186	yellow	B	>300	yellow
3-nitro	175	yellow	B	>300	orange-yellow
3,5-di-iodo	196	yellow-white	A	>300	yellow

* A—soluble in common organic solvents and alkalis, but insoluble in acids.
B—soluble in most polar organic solvents, ammonia and alkalis, but practically insoluble in non-polar organic solvents and acids.

presence of excess of hydrazine the azines are practically the only products. However, the aromatic hydrazones can be readily isolated by using a slight excess of hydrazine. Though salicylaldehyde hydrazone[8–11] and salicylaldazine[4–6] have been prepared and their metal complexes studied, very little work has been done on the condensation of substituted salicylaldehydes and hydrazine. Patwardhan *et al.*[7] have reported on the Ti(IV) chelates of azines prepared from 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde but gave details only for salicylaldazine. Torrey and Brewster[4] prepared and studied hydrazones of oxyaldehydes and ketones, but found only azines when hydrazine was used. At 100° 5-bromosalicylaldazine changes colour from pale yellow to orange, and this was confused with its melting point in the chemical abstract, though the original paper says the compound sinters at 301° and decomposes at 305–307°.

Likewise, the only hydrazone of a substituted salicylaldehyde mentioned in the old literature[15] is 3,5-di-iodosalicylaldehyde, which is said to decompose at 200°. The same m.p. (200°) is given for 3,5-di-iodosalicylaldazine in Beilstein.[16] Our work shows that the hydrazone decomposes at 196°, but the azine is stable up to 300°.

In optimization of the formation of hydrazones and azines, it has been found that for the former, the substituted salicylaldehyde should be added to the hydrazine, and for the latter, the order should be the reverse, *i.e.*, hydrazine should be added to the substituted salicylaldehyde. The reaction is exothermic and dropwise addition is therefore required, with either cooling or sufficient dilution with alcohol to carry out the reaction smoothly. The contents may then be refluxed on the water-bath.

The hydrazones and azines are separated by taking advantage of the fact that only the former are appreciably soluble in alcohol.

The extent of reaction appears to depend on the nature of the substituent group. An electron-attracting group (nitro- or halo-) is more favourable than an electron-releasing group for the formation of hydrazones. This agrees with the observations of Rao and Ratnam[17] on formation of mono-and di-substituted benziminazoles by the condensation of *o*-phenylene diamine and substituted aromatic aldehydes.

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PRELIMINARY COMMUNICATION

A NEW CHELATE-FORMING RESIN BEARING MERCAPTO AND AZO GROUPS

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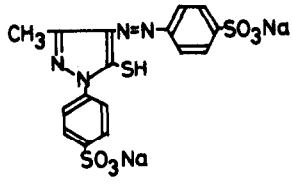
A chelate-forming resin bearing dithizone as the functional group was proved to be effective for selective collection of mercury(II) even from strongly acidic medium, as reported briefly.[1] The resin (called DzS resin hereafter) was prepared simply by mixing a solution of the sulphonic acid derivative of dithizone (denoted by DzS hereafter) with a common anion-exchange resin. After the adsorption of mercury(II), the DzS resin could be recovered almost completely by treatment with thiourea, and used repeatedly.[2] Thus ease of preparation and recovery, and good selectivity, characteristics desirable in a chelating resin, are features of DzS resin. However, no commercially available thiol-containing chelating resin possesses these features simultaneously. The high exchange-capacity of the anion-exchange resin for DzS and the high stability of DzS resin are considered to be due to the ion-exchange reaction between the sulphonic acid groups of DzS and the resin and the physical adsorption of DzS on the anion-exchange resin.

In further search for effective chelate-forming resins for collection of heavy metal ions, based on properties similar to those of DzS resin, synthesis of a new chelating agent, which bears mercapto and azo groups as a chelate-forming site and a sulphonic acid group as functional group for ion-exchange was planned, and azothiopyrine sulphonic acid (abbreviated to ATPS hereafter), which is a derivative of thiopyrine previously reported as a complexing agent,[3] was synthesized. The chemical structure of ATPS was confirmed by ultraviolet and NMR spectra and elemental analysis ($C_{16}H_{12}O_6N_4S_3Na_2$ requires C 38.55%, H 2.43%, N 11.24%; found C 37.9%, H 3.0%, N 10.7%). ATPS is a kind of thiol but unusually stable in solution, probably because of hydrogen bonding between the mercapto and azo groups. The synthesis, chemical properties and the complexation reactions of ATPS will be published elsewhere in detail, together with those of azothiopyrine, which is the first example of a chelating agent bearing mercapto and azo groups that has been obtained in pure state. A chelate-forming resin was easily prepared by stirring the anion-exchange resin (Amberlite IRA 400, 100–200 mesh) in a solution of ATPS, similarly to the preparation of DzS resin. The exchange-capacity of ATPS was found to be 1.3 mmole/g of resin, which is comparable to that of DzS resin. For loading of sufficient ATPS to give a practically useful ATPS resin, stirring for 60 min was found to be enough. The absorbance at 395 nm, λ_{max} for ATPS, was measured to determine the amount of ATPS in the solution in these experiments. In the

course of the ion-exchange reaction, the equivalent amount of chloride released indicated the presence of two sulphonic acid groups in a molecule of ATPS and the occurrence of the ion-exchange reaction on these groups. ATPS was found to be retained on the resin even when exposed to 1M sodium chloride, 0.5M hydrochloric acid and 1M sodium hydroxide, as shown in Fig. 1. These results indicate that both ion-exchange and physical adsorption may contribute effectively to the high exchange-capacity of ATPS and the high stability of ATPS resin, as in the case of DzS resin.

Effective adsorption of mercury(II) on ATPS resin in column operation was proved by the break-through curve shown in Fig. 2. When 0.1M nitric acid containing 50 ppm of mercury(II) was passed through a 10 x 100 mm column, the concentration of mercury(II) in up to 1 litre of effluent could be reduced to as low as 0.5 ng/ml by the use of ATPS resin (capacity 0.2 mmole/g of resin).

ATPS resin may be expected to be very useful as a chelating resin for the collection of mercury(II) and probably also for other metal ions. Detailed studies on the properties of ATPS resin and its application to the collection of various metal ions are now under way.



ATPS [disodium 4,4'-(4-diazenediyl-5-mercapto-3-methyl-1,2-diazacyclopenta-2,4-diene-1-yl)dibenzenesulphonate]

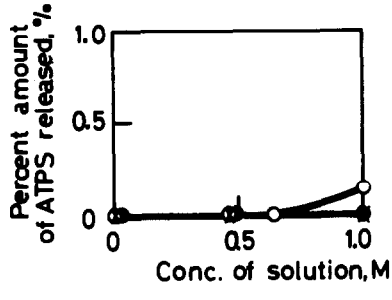


Fig. 1. Release of ATPS from anion-exchange resin. Fifty mg of ATPS resin (0.2 mmole/g of resin) was introduced into a flask containing 5 ml of solution, and ATPS released into the solution was in 24 hr at 20-22° determined spectrophotometrically. o HCl, x NaCl, • NaOH.

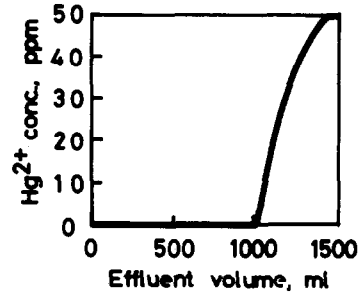


Fig. 2. Break-through curve for ATPS-Hg^{2+} system. Flow-rate, 60 ml/hr.

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INTERFERENCE IN ANODIC STRIPPING VOLTAMMETRY FROM THE TEFLON VESSELS USED IN PRESSURIZED DIGESTION

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Summary—The insufficient inertness of Teflon vessels towards acids at high temperature and pressure is shown to be the source of some interferences in anodic stripping voltammetry. To avoid such problems the use of Pyrex glass inserts in Teflon-lined steel bombs is proposed for the determination of non-volatile heavy metals. The procedure is easily applied to commercially available digestion bombs. Blank values and recovery tests for blood samples spiked with Cd, Pb and Cu are given, and the completeness of the digestion has been checked.

In recent years, bombs for pressurized acid digestion have found widespread use in the determination of trace metals in organic and inorganic materials.[1–7] The main advantage of this method is the relatively fast digestion of the sample, and the very low reagent blanks. It has been shown that losses of trace elements are negligible even for the volatile elements.[4,8] Teflon-lined steel bombs of different designs have been developed;[1,3,4,9] the bombs are mainly used to decompose inorganic material such as geological samples, and biological materials.

Electrochemical techniques such as differential pulse anodic stripping voltammetry (DPASV) are relatively seldom used in connection with acid-digestion under pressure. The main reason is that samples with a high organic content are not completely mineralized when nitric acid is used.[6,7,10] In addition the formation of electroactive nitrated substances leads to high background currents and interfering signals, which disturb the determination of heavy metals.[7] Therefore the use of acid mixtures in the bomb and an additional digestion step after the decomposition under pressure are often necessary.[7] On the other hand acid-digestion under pressure may be a suitable technique for certain inorganic samples,[2,5] which have a relatively low content of organic material.[11]

The sample vessels are normally made from Teflon. It is well known that Teflon is not completely inert towards acids at elevated temperatures and pressures. After a few digestions the surface is corroded by the acid.[12]

This paper describes the influence of the decomposition products of Teflon on the determination of heavy metals by DPASV. It is shown that the interferences can be avoided by placing Pyrex glass inserts inside the Teflon crucibles. This procedure can be used for nearly all commercially available systems, when non-volatile heavy metals such as Zn, Cd, Pb and Cu are determined. No loss of metals by adsorption has been found. The blank values obtained are similar to those for Teflon crucibles used under routine method conditions (see also ref. 7). The completeness of the digestion with acid mixtures in glass inserts in the bomb has been checked with different types of biological material.[11,16] The glass insert is easy to remove from the bomb and allows the evaporation of the remaining acid on a thermostatically controlled hot-plate with a simple dust protection, so that expensive equipment for evaporation directly in the Teflon vessels is not needed.[13]

EXPERIMENTAL

Apparatus

A home-made digestion bomb similar to that of Tölg *et al.*[4] and a thermostatically controlled heating block with water cooling, which could accommodate 5 bombs, were employed. Teflon vessels with 24 mm outer diameter and 83 mm height were used. The wall thickness was 4.5 mm and the inner volume 10.6 ml (see Fig. 1a). The glass inserts, with an outer diameter of 14–14.5 mm, a height of 50 mm and a wall thickness of 1 mm, were made of Pyrex. The volume was approximately 5 ml. A glass bar was fused on, over the opening, to facilitate the removal of the glass insert from the Teflon crucible by means of a glass hook (Fig. 1b). To evaporate the remaining acid a thermostatically controlled hot-plate and an aluminium block, which could accommodate 4 glass inserts (Fig. 1c), were used. A glass funnel with a wide stem served as dust protection. The circulation of the hot air prevented the contamination of the samples by dust.

The measuring equipment for DPASV was similar to that reported previously[11] and consisted of a Princeton Applied Research 174A Polarographic Analyzer with a Radiometer REC 51/REA 112 recorder and a home-made timer unit. A Metrohm EA 410 hanging mercury drop electrode, an Ag/AgCl reference electrode with gel-stiffened internal electrolyte[14] and a platinum coil counter-electrode were used. The glass capillary of the HMDE was siliconed with hexamethyldisilazane (Fluka AG).[14] Ultrapure water was made by using a Millipore "Milli-Q" water-purification system.

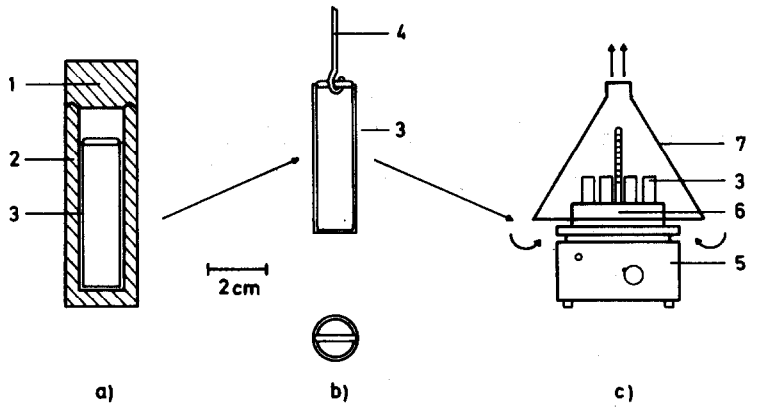

Fig. 1. (a) Teflon crucible with Pyrex glass insert; (b) the glass insert and how to remove it; (c) experimental set-up for the evaporation of the acids. 1, Teflon cover; 2, Teflon container; 3, Pyrex glass insert; 4, glass hook; 5, thermostatically controlled hot-plate; 6, aluminium block for 4 inserts; 7, glass funnel as dust protection.

Reagents

All reagents used were of high purity (Merck "Suprapur"). The acetate buffer consisted of an equimolar (0.1*M*) mixture of acetic acid and sodium acetate. Standard metal solutions were prepared from analytical-grade chloride salts.

Procedure

All glass equipment was cleaned thoroughly with chromic/sulphuric acid and dilute nitric acid before each series of experiments. The polyethylene tips of the micropipettes were soaked for one week in dilute nitric acid; the solution was changed twice. Afterwards the tips were rinsed with distilled water and dried at 40°.[15] Teflon crucibles and glass inserts were cleaned with 0.8 ml of 65% nitric acid at 190° under pressure for 2 hr before each experiment (see also ref. 7). New equipment was cleaned several times before use.

For the determination of the blank 0.8 ml of 65% nitric acid or a mixture of nitric, perchloric and sulphuric acids (2 + 1 + 1) was placed in the Teflon crucible or in the glass insert. After a decomposition time of 2 hr at 190° the acid was evaporated from the Teflon container by replacing the open bomb in the water-cooled heating block at a temperature of 150°. Purified nitrogen was passed over the acid to accelerate the evaporation and to avoid contamination by dust. The acid was evaporated from the Pyrex glass inserts by placing them in the aluminium block on the hot-plate. The residue was redissolved in 5 ml of acetate buffer (pH 4.6) or in 0.05 ml of 30% hydrochloric acid and 4 ml of water and then transferred to the electrolytic cell. The solution was deaerated for 10 min with highly purified nitrogen, a fresh mercury drop was extruded and the stirrer started. After an electrolysis time of 5 min at −0.8 V *vs.* Ag/AgCl, the stirrer was stopped and the stripping voltammogram of Cd, Pb and Cu was recorded after a waiting time of 30 sec. The following parameters were used: scan-rate 10 mV/sec, pulse repetition time 0.195 sec (obtained by a modification of the instrument) and modulation amplitude 50 mV.

The completeness of the digestion was checked with 0.4 ml of blood and 0.8 ml of the acid mixture. The digestion procedure was a slight modification of that described above. For details see ref. 16.

Sample digestion was carried out overnight under the necessary safety precautions for steel bombs. Only small amounts of perchloric acid (0.2 ml) were used together with 0.2 ml of sulphuric acid, to lower the risk of explosion during uncontrolled evaporation.[17] During all the experiments no irregularities could be observed. This is in agreement with earlier investigations using perchloric acid in steel bombs.[6,7] However, the risk of explosion can never be totally excluded, even when nitric acid is used.

To assess losses of metals by adsorption onto the walls of the glass inserts, 0.4 ml of blood or 0.8 ml of nitric acid was spiked with known amounts of Cd, Pb and Cu and treated in the same way as described above.

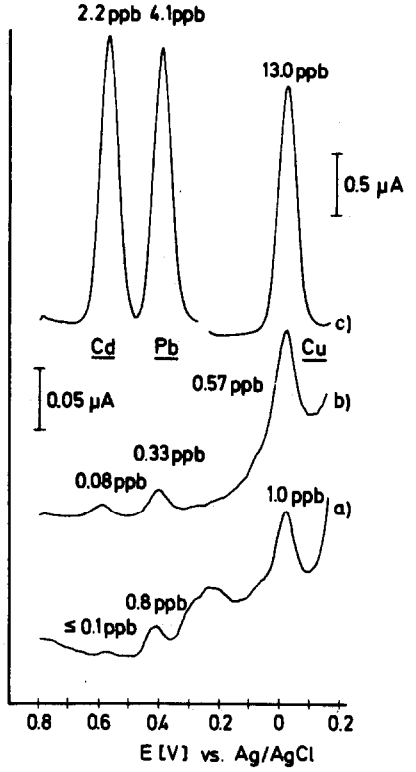

Fig. 2. Stripping voltammograms obtained after sample pretreatment in different digestion bombs. Samples were diluted with 0.1*M* acetate buffer (pH 4.6). (a) Blank obtained with 0.8 ml of nitric acid in the Teflon vessel. (b) Blank obtained with a glass insert in the Teflon crucible. (c) Digestion of a spiked sample in the glass insert.

Table 1. Blank values for the digestion bomb used with glass inserts in the Teflon vessels

	Blank obtained with 0.8 ml of HNO_3					Blank of the digestion procedure for blood samples with 0.8 ml of acid mixture				
		Mean $\bar{x}$,		s_D,	s_R,		Mean $\bar{x}$,		s_D,	s_R,
Metal	n	*ppM**	*ng*	*ng*	%	n	*ppM*†	*ng*	*ng*	%
Cd	7	0.07	0.35	0.1	29	4	0.039	0.16	0.04	25.0
Pb	7	0.48	2.4	0.6	25	4	0.44	1.76	0.20	11.4
Cu	7	0.76	3.8	0.9	24	4	0.31	1.24	0.32	25.8

* After dilution to 5 ml with 0.1 *M* acetate buffer.
† After dilution with 0.05 ml of 30% HCl and 4 ml water.

RESULTS AND DISCUSSION

DPASV offers a low-cost possibility for determining trace metals in the ppM-range (μg/l.) and below. However, the main disadvantage of this method is the high susceptibility to trouble from organic impurities of various origins. The relatively difficult handling of the earlier types of hanging mercury drop electrodes has led to a rather limited use of this method in comparison to atomic-absorption spectrometry. As the origin of interfering substances the following sources may be considered:

—insufficient washing of the equipment (also surface active substances)
—the procedure for siliconing the capillary and the electrolytic cell
—incomplete digestion of the sample.

The last source often predominates for organic samples. However, the use of low-temperature ashing[15] or acid digestion with nitric/perchloric/sulphuric acid mixtures under pressure normally gives a satisfactory decomposition of the sample.[7,16]

Even so, interfering signals and decreased sensitivity were observed in the determination of heavy metals in inorganic samples such as hydroxyapatite after the digestion under pressure in a Teflon-lined steel bomb. The same type of interference was obtained in the determination of the blank values (see Fig. 2a). This, and the clearly visible corrosion of the Teflon walls by nitric acid[12] and other acids indicates that the interferences were probably caused by decomposition products of the Teflon.

To examine this phenomenon more closely, the determination of blank values was repeated with Pyrex glass inserts in the Teflon crucibles (see experimental section). As shown in Fig. 2b, a high sensitivity and a background without any interfering signals were obtained. Also, reasonably low blank values were obtained by using the glass inserts (see Table 1). Under routine conditions the metal blank values were similar for Pyrex glass and quartz inserts and for the Teflon vessels. In addition the same blank values were obtained for nitric acid and for the acid mixture. Figure 3 shows typical voltammograms.

To discover possible losses of metals by adsorption, samples were spiked with different known amounts of Cd, Pd and Cu. Table 2 shows that no significant losses occurred. The loss of nitric acid by condensation onto the cover and in the space between the glass insert and the Teflon crucible was about 2%. No significant increase in the recovery was observed

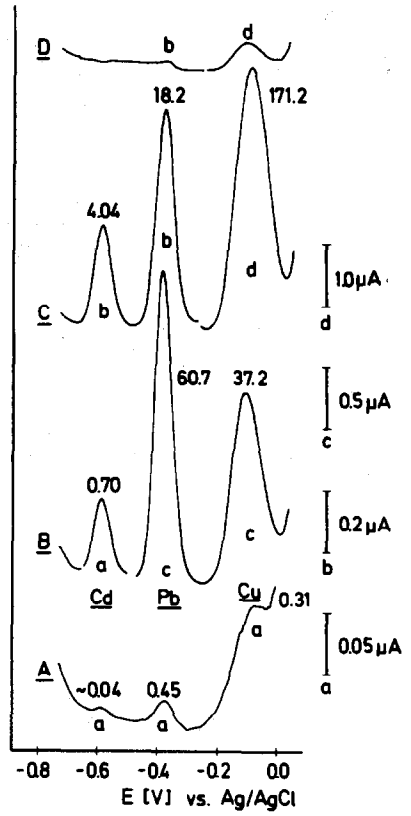

Fig. 3. Stripping voltammograms of digested blood samples.[16] Blood (0.4 ml) was decomposed with 0.8 ml of the acid mixture, in the glass insert in the bomb. After heating to dryness, samples were diluted with 0.05 ml of 30% HCl and 4 ml of water. The small letters below the signals mark the measuring range, and the numbers above, the concentrations in ppM (parts per milliard). A, Blank for the digestion procedure in the glass insert; B, sample from a person exposed to lead; C, blood sample with low metal content, after spiking; D, background current of C with zero electrolysis time.

Table 2. Recovery of digestion in bomb with glass inserts in the Teflon vessels: 0.4 ml of blood was spiked, digested and diluted with 0.05 ml of 30% HCl and 4 ml of water; values are given for the diluted samples

Metal	Sample content				Quantity added, ng	Quantity found			Recovery, %
	n	$\bar{x}$ ppM	$\bar{x}$ ng	s_D ng		n	$\bar{x}$ ng	s_D ng	
Sample 1									
Cd	3	0.29	1.16	0.11	15.7	3	15.1	0.6	96.2
Pb	4	9.9	40.4	1.4	29.0	4	28.2	1.8	97.2
Cu	4	86.4	350.0	27.0	317.7	3	314.0	10.8	98.8
Sample 2									
Cd	4	0.58	2.36	0.35	11.2	4	11.4	0.7	101.8
Pb	4	57.2	231.6	10.2	103.6	4	106.0	6.8	102.3
Cu	4	36.9	149.6	6.7	317.7	4	316.8	31.7	99.7

when the Teflon crucible and cover were rinsed with small amounts of acetate buffer (pH 4.6) and the rinsings were added to the digestion solution. However, small signals of interfering impurities were sometimes observed in this case.

When the present technique is used, the determination of non-volatile heavy metals by DPASV can be performed without the problems described above. The use of glass inserts is considerably less expensive than the recently introduced glassy carbon crucibles.[19] Another advantage of the glass inserts is the easy removal of the digested solution from the Teflon vessel.

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DETERMINATION OF SULPHUR FUNCTIONS WITH *N*-IODOSUCCINIMIDE

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Summary—Titrimetric determination of thioureas, thiols, xanthates and dithiocarbamates with *N*-iodosuccinimide (NIS) is described. The method for xanthate can be applied to carbon disulphide (converted into xanthate with potassium ethoxide). Acidic and non-aqueous solutions of the oxidizing agent are stable. The procedures are rapid and accurate to 0.1% with a precision of 0.2%. Hydrogen sulphide and thiocarbonyl compounds interfere. The behaviour of *N*-bromosuccinimide and NIS with thiols in aqueous medium is compared. It is shown that iodine is the oxidizing species in both cases. The limitations of iodine as a reagent for thiol determination are discussed. Cysteine, which cannot be determined with iodine, can be determined with NIS. The role of methanol in non-aqueous determination of thiols is discussed. Methanol accelerates the oxidation, which is otherwise slow in acetonitrile medium.

Thioureas are biologically, commercially and medicinally important compounds.[1,2] Several approaches for their determination have been reviewed.[3–6] *N*-Bromosuccinimide has been found to desulphurize thioureas in presence of potassium bromide.[5] As a part of a project on the determination of sulphur-containing organic compounds through their functional groups, reactions of *N*-iodosuccinimide (NIS) have been investigated and methods evolved for the determination of these sulphur functions. NIS is found to oxidize thioureas readily and quantitatively to formamidine disulphides according to the general equation.

$$2RNHC(NH_2)=S + (CH_2CO)_2NI \rightarrow [RNHC(=NH)S-]_2 + (CH_2CO)_2NH + HI$$

In presence of mercuric chloride the following stoichiometry was found.

$$RNHCSNH_2 + (CH_2CO)_2NI + H_2O \rightarrow RNHCONH_2 + (CH_2CO)_2NH + S + HI$$

The wide distribution of the sulphydryl group makes the study of thiols important. The many methods available for the determination of thiols have been reviewed.[7–9] Interhalogens,[10] *N*-haloamines, *N*-haloamides,[11] periodate,[12] chloramine-T and chloramine-B[13] have been successfully employed for the assay of thiols. The classical method for the estimation of cysteine by iodine has been improved.[14] Recently, thiols in general and cysteine in particular have been estimated with *o*-diacetoxyiodobenzoate[15,16] and ferricyanide.[17] *N*-Bromosuccinimide (NBS) in the presence of acid and potassium iodide has been proposed for determination of thiols, including 3-mercaptopropionic and mercaptosuccinic acid.[18] In the presence of acid and potassium iodide the reactions of NBS are essentially those of iodine. Danehy and Oester[19,20] have discussed in detail the limitations of iodine for the determination of such thiols and cysteine. In a systematic study on the determination of sulphydryl compounds, consideration has been given to the behaviour of NIS and NBS, which have similar structures, towards thiols. NIS has aroused a great deal of interest in synthetic organic chemistry. Solutions of NBS are unstable and liberate bromine on keeping, but NIS is very stable in acidic as well as non-aqueous media. Conditions have been found for quantitative oxidation of cysteine to cystine, by varying the pH and iodide concentration.

The utility of xanthates has been widely discussed.[21,22] Numerous methods[23–28] dealing with the dithiocarbonate functional group are primarily concerned with the determination of a specific alkyl xanthate in the presence of impurities, *e.g.*, sulphides. NIS oxidizes xanthates to dixanthogens. The titration is done in methanol with an acetonitrile solution of NIS or in neutral aqueous medium. The procedure can be applied to carbon disulphide after its conversion into xanthate with potassium ethoxide:

$$CS_2 + C_2H_5OH \rightarrow C_2H_5OCSSK$$

Formation of xanthate by this reaction is quantitative provided that significant amounts of water are absent.

The analytical importance of dithiocarbamates has been reviewed.[29,30] Various reactions for their detection[31] and determination[32] have been discussed. Although hypoiodite quantitatively oxidizes dithiocarbamates derived from primary amines, non-stoichiometric results are obtained for those derived from secondary amines.[29] Of the methods proposed, direct titration with iodine[33–35] appears to be the best, but in aqueous medium the thiuram disulphide formed hampers the end-point. Linch[33] proposed titration

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with iodine in ethanolic solution, the appearance of iodine being taken as the end-point, but the colour is fugitive and over-titration is required for a definite end-point. The method is rapid but furnishes only approximate results. The mercurimetric method[36] is excellent only for dithiocarbamates derived from secondary amines. *N*-Iodosuccinimide quantitatively oxidizes dithiocarbamates in non-aqueous medium to thiuram disulphides:

$$2R_2NCSSK + (CH_2CO)_2NI \rightarrow (R_2NCSS-)_2 + (CH_2CO)_2NK + KI$$

Samples are titrated in methanol with acetonitrile solution of the reagent.

EXPERIMENTAL

Reagents

N-Iodosuccinimide was prepared by the method of Djerassi and Lenk.[37] A 0.02*M* solution was prepared by dissolving the compound in dilute hydrochloric acid or acetonitrile, filtering off any insoluble residue, diluting and standardizing iodimetrically. It was kept in the dark.

Samples

Most of the thiols were used as received from Evans Chemetics, New York, and the sodium diethyldithiocarbamate was also a commercial product. Thioureas, xanthates and the other dithiocarbamates were prepared and purified[38] by the author. All other chemicals used were of reagent grade.

Thioureas in aqueous medium

Procedure A. Samples containing 0.01–0.1 meq of the thiourea group were used. For alkylthioureas the sample was dissolved in water and enough sulphuric or hydrochloric acid was added to make the acid concentration 1*N*. Aryl derivatives were dissolved in 10–15 ml of 18*N* sulphuric acid, which was diluted to 3.5*N* and cooled just before the titration. One ml of 1% starch solution was added as indicator, for visual end-point detection. Potentiometric titrations were done as described for procedure B.

Procedure B. An aliquot of aqueous alkylthiourea solution containing about 0.1 mmole of sample was treated with 5 ml of saturated aqueous mercuric chloride solution and 5 ml of chloroform, and titrated with 0.05*N* *N*-iodosuccinimide. Appearance of the colour of iodine in the chloroform served to indicate the end-point.

For potentiometric titration, no chloroform was added and a modified calomel or antimony electrode was used as reference electrode and a bright platinum wire as indicator electrode.

L-*Cysteine and α-substituted* D- *or* L-*cysteines*

A portion of test solution was added to sufficient phosphate buffer to maintain the pH at 7 during the titration and 1 g of potassium iodide was added. The mixture was titrated with NIS until a slight yellowing of the solution occurred. Then 1 ml of starch solution was added, and the titration continued to a blue end-point that persisted for 30 sec.

Thiols in aqueous medium

A sample containing 0.1–1.0 meq of thiol was dissolved in 30–50 ml of water. For water-insoluble thiols 5–10 ml of glacial acetic acid were used to dissolve the sample, and twice as much water was added just before the titration. One ml of 1% starch and 2 ml of 4% acetic acid were added, and the solution titrated with NIS to a blue end-point. Alternatively, a potentiometric titration was done, with an antimony or modified calomel reference electrode and a bright platinum wire as indicator electrode.

Xanthates in aqueous medium

A sample containing 0.1–1.0 meq of the sodium or potassium xanthate was dissolved in 30–50 ml of water, 1 ml of 1% starch solution was added and the solution was titrated with NIS.

The dixanthogen precipitates as it is formed but does not affect the reaction or the end-point. The mixture should be shaken vigorously during the titration.

Carbon disulphide in aqueous media

A sample containing 0.1–1.0 meq of carbon disulphide was weighed in a small sealed glass bulb and placed in 0.5–2.0 ml of 10% potassium ethoxide solution and 5 ml of absolute ethanol in a 150-ml conical flask. A sharp rap against the sides of the flask was sufficient to break the bulb and release the sample. The contents were swirled for 2 min, then the flask was cooled in an ice-bath and 30 ml of water and 2–3 drops of phenolphthalein indicator were added. The solution was just acifidied with 1*M* acetic solution and the potassium ethyl xanthate formed was titrated with NIS as described for xanthates.

Thiols in non-aqueous media

A sample containing 0.1–1.0 meq of mercapto group was dissolved in 30 ml of methanol containing 50 mg of potassium iodide. The solution was titrated with 0.05*N* NIS in acetonitrile, the end-point being indicated by the appearance of the colour of iodine or potentiometrically. Enough methanol must be added for it to constitute about 80% of the total solvent at the end-point.

Dithiocarbamates and xanthates in non-aqueous media

A sample containing 0.1–1.0 meq of –CSSK group was dissolved in 40 ml of methanol; 50 mg of potassium iodide were added and the solution was titrated with 0.05*N* NIS in acetonitrile from a microburette provided with a guard tube to keep out atmospheric moisture. The end-point was detected by the appearance of a yellow tint or potentiometrically.

RESULTS

Some typical results are summarized in Tables 1 and 2. Cysteine, methionine, and thiourea interfere seriously in all the procedures, while acetaldehyde (75:1), allyl alcohol (100:1) and diacetone alcohol (40:1) give results that are 3.5% low, and 4% and 6% high respectively, when present in the molar ratio to determine and that is shown in parentheses. Serine, glycine, alanine, glutamic acid, valine, glutamine, proline, leucine, threonine urea, acrylonitrile, dimethylsulphoxide, dibenzyl sulphide, thiophene and diphenyl disulphide (0.5 mmole) do not interfere.

Unlike the aqueous solution, the acetonitrile solution of NIS does not liberate molecular iodine on storage (for at least 7 days at 20°). The burette should be fitted with a guard-tube to protect the oxidant from atmospheric moisture.

DISCUSSION

NIS has been reported[18] to react stoichiometrically with mercaptosuccinic and *o*-mercaptobenzoic acids,

Table 1. Determination of thioureas, dithiocarbamates and xanthates with *N*-iodosuccinimide

Sample	Purity, %		Comparison method	Average deviation, %
	Present method*			
	Visual	Potentiometric		
Thiourea	98.5	99.8	99.7[a]	0.1
Thioureas				
N,N'-Dimethyl	97.0	97.1	97.2[a]	0.2
Butyl	99.6	99.7	99.4[a]	0.3
Allyl	98.7	98.8	98.9[a]	0.2
Isoamyl	96.5	96.5	96.2[a]	0.3
Phenyl	96.4	96.2	96.1[b]	0.2
o-Tolyl	97.6	97.3	97.4[b]	0.2
o-Ethoxylphenyl	98.3	98.2	98.5[b]	0.3
Na and K dithiocarbamates				
Dimethyl	76.6	76.8	76.5[c]	0.2
Di-isopropyl	88.6	88.4	88.4[d]	0.4
Phenylethyl	83.3	83.0	83.1[c]	0.3
Diamyl	93.8	93.7	93.9[c]	0.2
Tetraethyl	82.5	82.6	82.3[d]	0.3
Na and K xanthates				
Methyl	99.8	99.8	99.6[d]	0.2
Isopropyl	99.7	99.6	99.8[c]	0.1
Allyl	99.5	99.6	99.4[d]	0.2
Cyclohexyl	99.4	99.5	99.2[c]	0.3
Benzyl	99.6	99.7	99.4[d]	0.3

* Average of 10 determinations.
a Sodium hypoiodite[3]
b Iodine titration[3]
c Mercurimetric titration[23,36]
d Iodine titration[36]

these results being compared with those from the iodine titration[39] method, but others have found that neither NBS nor NIS is suitable for determination of these two acids and 3-mercaptopropionic acid, there being a variable positive error.

In our opinion, iodine is the oxidizing species in

Table 2. Determination of thiols with *N*-iodosuccinimide

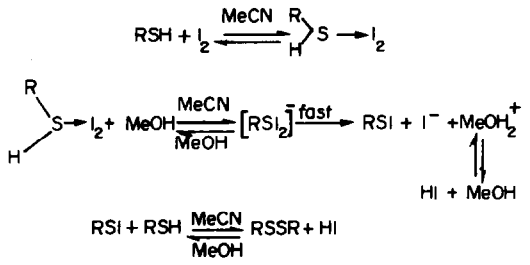
Sample	Purity, %		Comparison method	Average deviation, %
	Present method*			
	Visual	Potentiometric		
L-Cysteine and α-substituted DL-cysteines	99.1	99.3	99.4[a]	0.4
Ethane thiol	97.9	98.0	98.1[b]	0.2
Glutathione	97.9	97.6	97.8[c]	0.3
2-Mercaptopropionic acid	96.7	96.2	96.6[b]	0.2
2-Diethylaminoethane thiol hydrochloride	98.1	98.5	98.2[d]	0.2
Benzyl mercaptan	96.1	98.0	98.2[c]	0.3
Thioglycollic acid	80.5	80.5	80.3[a]	0.1
Thiobenzoic acid	94.9	95.2	95.0[b]	0.2
2-Mercaptobenzothiozole	97.6	97.5	97.5[e]	0.5
Methyl 3-mercaptopropionate	96.3	96.2	96.0[b]	0.2
Benzene thiol	99.2	98.8	99.0[e]	0.2
2-Naphthalene thiol	98.9	99.4	99.1[e]	0.3
Glycerol-1-thiol	88.1	80.0	79.7[a]	0.2
Cyclohexane thiol	99.4	99.5	99.8[b]	0.5
1-Pentane thiol	88.6	88.2	88.4[b]	0.2

* Mean of 10 determinations.
a *o*-Diacetoxyiodobenzoate[15]
b Iodimetry[39]
c Iodimetry[43]
d Iodine monochloride titration[10]
e Mercurimetry[23]

NBS titrations in which potassium iodide is added as additional reagent. NBS contains unstably bound bromine and it might be assumed that the actual oxidizing agent is either hypobromous acid formed by hydrolysis of NBS, or Br^+, but this is not so because oxidation of thiols with bromine is known to be non-stoichiometric.[40] The amino group in 2-mercaptoethylammonium chloride or glutathione remains intact and *N*-bromosuccinimide attacks only the sulphur atom. Moreover, in the present determinations glycine, alanine and serine do not interfere. This further indicates that bromine is not the oxidizing species in *N*-bromosuccinimide titrations.

Danehy[19,20] studied thiol–iodine reactions and suggested that a carboxyl group on a carbon atom β to the thiol group causes an intramolecular displacement reaction and that a five-membered cyclic intermediate is formed. This intermediate can undergo further oxidation to sulphenic acid and higher oxidation states instead of forming the disulphide, which vitiates the titration. On the other hand, thiols such as 2-mercaptopropionic, mercaptoacetic and *m*- and *p*-mercaptobenzoic acids without a β-carboxyl group give the correct stoichiometry. Finally glutathione shows minimal tendency to be over-oxidized because the mercapto group is too remote from the carboxyl groups.

Although in acetonitrile or glacial acetic acid, either alone or mixed, the reactions of thiols with *N*-iodosuccinimide are slow and iodine appears during the course of titration, in methanol either alone or mixed with acetonitrile (about 80% methanol at the end-point), the reactions are instantaneous and the end-points accurate. The function of the methanol is to deprotonate the complex.



This scheme has the merit of suggesting that if it is the basicity of methanol which induces the reaction chain, then a more basic species should fulfil this function even more effectively. It may be mentioned here that pyridine is used as catalyst in the titration of thiols with iodine in benzene medium.[44]

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PHOTOMETRIC REAGENTS FOR ALKALI METAL IONS, BASED ON CROWN-ETHER COMPLEX FORMATION—III*

4′-PICRYLAMINOBENZO-15-CROWN-5 DERIVATIVES

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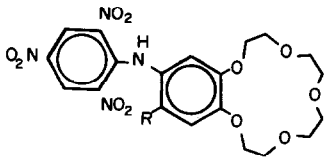
Summary—An extraction study of alkali metal cations has been made with crown-ether reagents, 4′-picrylaminobenzo-15-crown-5 derivatives (HL). On dissociation in alkaline medium, the orange HL gives the blood-red anion L^- and extracts alkali metal ions into chloroform as coloured complexes of composition ML.HL or ML. The ease of extraction decreases in the order, $K^+ > Rb^+ > Cs^+ > Na^+ \gg Li^+$. The extracted complexes are ML.HL for K^+ and Rb^+, and both ML.HL and ML for Na^+. The Li^+ complex is not extracted. The photometric determination of 10–800 ppm of K^+ is possible in the presence of other alkali and alkaline earth metal ions.

Crown ethers or cryptands are known as selective neutral ligands for various alkali or alkaline earth metal ions and some of the cationic metal complexes are readily extractable from the aqueous into an organic phase. The selectivity principally depends on the cavity size within the ligand molecule,[1–4] and several extraction studies on specific metal ions are described in the literature.[5–8] In such extraction studies, bulky or lipophilic anions are usually preferred as the pairing anion, and some of them are highly coloured, *e.g.*, the picrate anion. The fact that the extracted complex is coloured immediately suggests that the applications may be extended to include extractive photometric determination of alkali metal ions, but rather surprisingly few publications have been concerned specifically with this.[9] On the other hand, if a light-absorbing anion is incorporated into the ligand molecule, a new series of photometric reagents for alkali or alkaline earth metal ions should be realized.[10] Chromogenic complexing reagents which show a distinct colour change on interaction with alkali metal ions are practically unknown.[11]

In the absence of satisfactory photometric methods, traces of alkali metal ions are generally determined by techniques based either on potentiometry or atomic spectra. However, we believe that the photometric method still deserves extensive exploration, first in its own right from the methodological point of view and secondly to broaden the choice of method for individual samples in practical alkali metal analysis. The present series of studies is devoted to this aim mainly through the two types of approach outlined above, *i.e.*, ion-pair extraction of the conventional crown-ether cation complex with an anionic dye and the development of specifically designed chromogenic crown-ether reagents for alkali metal ions. In this report, the synthesis of 4′-picrylamino-



1 : R=H
2 : R=NO_2
3 : R=Br

benzo-15-crown-5 derivatives (HL: **1**, R = H; **2**, R = NO_2; **3**, R = Br), first chromogenic reagents for alkali metal, and their application to the photometric determination of 10–800 ppm of K^+ are described. Part of the work has been published in a preliminary note.[10]

EXPERIMENTAL

Synthesis

1. 4′-Nitrobenzo-15-crown-5 (0.50 g) was catalytically reduced to 4′-aminobenzo-15-crown-5 in ethanol.[12] The crude product, after removal of the catalyst and the solvent, was redissolved in 2 ml of methanol, followed by the addition of picryl chloride (0.45 g). Sodium hydrogen carbonate (0.25 g) was then added in portions, and the mixture stirred at room temperature for 15 min. The deep red mixture was acidified with dilute hydrochloric acid and evaporated under reduced pressure, and the residue was extracted with chloroform. The chloroform layer, after evaporation, was chromatographed on a silica gel column (2 × 15 cm) with ether–chloroform (1:1, v/v) as eluent. The major band was collected, and the product was recrystallized from methanol, m.p. 155° (uncorrected). Yield, 570 mg (72%). Found: C, 48.5%; H, 4.4%; N, 11.2%. Calculated for $C_{20}H_{22}N_4O_{11}$: C, 48.59%; H, 4.49%; N, 11.33%. Electronic spectrum (Fig. 1): λ_{max} 395 nm; ϵ 1.08 × 10^4 l.mole^{-1}.cm^{-1} (chloroform, $c = 10^{-4}M$). pK_a, 10.55 [μ 0.10 (LiCl); 10% dioxan; 25°].

* Contribution No. 480 from the Department of Organic Synthesis, Kyushu University.

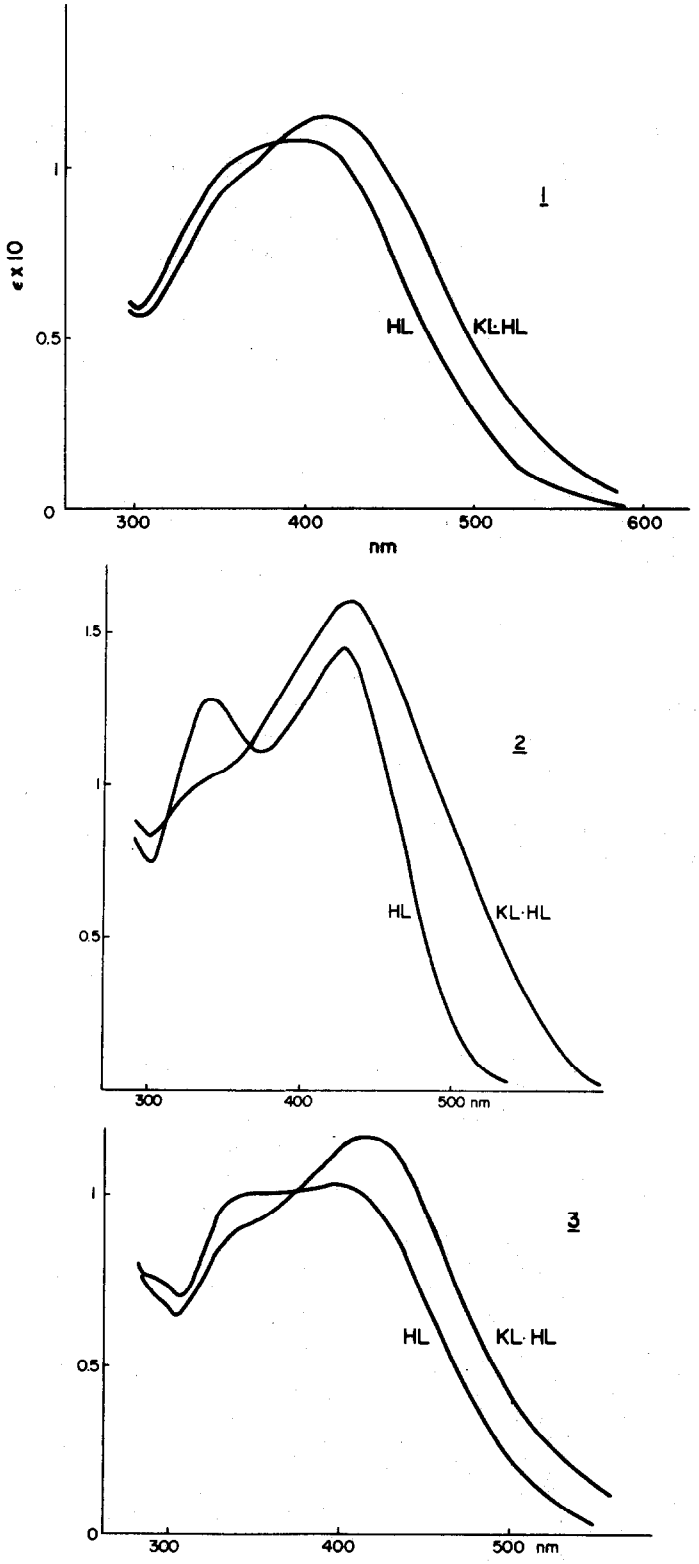


Fig. 1. Electronic spectra of HL and KL.HL in chloroform. Crown reagents **1**, **2** and **3**.

2. A mixture of acetic acid, chloroform and fuming nitric acid (s.g. 1.42) (0.5 ml each) was added dropwise to a chloroform solution (10 ml) of **1** (300 mg) at room temperature. After 10 min, the reaction mixture was washed with water (10 ml) four times and evaporated. The crude **2** obtained as an orange solid was recrystallized from acetone–water (1:2), m.p. 208–209° (uncorrected). Yield, 270 mg (82%). Found: C, 44.4%; H, 3.9%; N, 12.9%. Calculated for $C_{20}H_{21}N_5O_{13}$: C, 44.53%; H, 3.92%; N, 12.98%. Electronic spectrum (Fig. 1): λ_{max} 424 nm; ϵ 1.43×10^4 $l.mole^{-1}.cm^{-1}$ (chloroform, $c = 1 \times 10^{-4}M$). pK_a, 8.63 [μ 0.10 (LiCl); 10% dioxan; 25°].

3. Bromine (100 mg) was added to **1** (300 mg) in glacial acetic acid (2 ml). After heating at 80° for 10 min, the reaction mixture was cooled to room temperature, and the precipitate formed was filtered off. The product was recrystallized from chloroform–methanol, m.p. 216–217° (uncorrected). Yield, 210 mg (60%). Found: C, 41.5%; H, 3.6%; N, 9.6%. Calculated for $C_{20}H_{20}N_4O_{11}Br$: C, 41.90%; H, 3.69%; N, 9.77%. Electronic spectrum (Fig. 1): λ_{max} 402 nm; ϵ 1.02×10^4 l.mole^{-1}.cm^{-1} (chloroform, $c = 1 \times 10^{-4}M$). pK_a, 9.32 [μ 0.10 (NaCl); 20% dioxan].

Extraction study

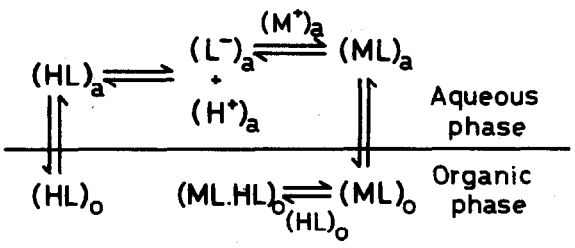
1. An aqueous solution of alkali metal salt (5 ml) was shaken with a chloroform solution (5 ml) of **1** ($1.83 \times 10^{-3}M$ unless otherwise noted) and triethylamine ($1.0M$) at 25°. After phase separation, the absorbance of the organic layer was measured at 560 nm in a 1-cm standard cell at 30° (Hitachi spectrometer type 200). In this medium, the pH of the aqueous layer was constant at 11.46.

2. An aqueous solution of alkali metal salt and triethanolamine ($0.5M$) (5 ml) was shaken with a chloroform solution (5 ml) of **2** in a similar manner to that described above. The absorbance was measured at 550 nm.

RESULTS AND DISCUSSION

Extraction equilibria

The effective equilibria in which **1** or **2** takes part are summarized in Scheme 1 and in expressions (1)–(5);



Scheme 1.

$$(HL)_a \rightleftharpoons (HL)_o \qquad :D_{HL} \qquad (1)$$

$$(HL)_a \rightleftharpoons (H^+)_a + (L^-)_a \qquad :K_a \qquad (2)$$

$$(L^-)_a + (M^+)_a \rightleftharpoons (ML)_a \qquad :K_{ML} \qquad (3)$$

$$(ML)_a \rightleftharpoons (ML)_o \qquad :D_{ML} \qquad (4)$$

$$(ML)_o + (HL)_o \rightleftharpoons (ML.HL)_o \qquad :K^{(o)}_{ML.HL} \qquad (5)$$

The extraction constants are defined by

$$(HL)_o + (M^+)_a \rightleftharpoons (ML)_o + (H^+)_a$$

$$K^{ex}_{ML} = K_{ML}K_aD_{ML}/D_{HL} = \frac{[(ML)_o][(H^+)_a]}{[(HL)_o][(M^+)_a]} \qquad (6)$$

and

$$2(HL)_o + (M^+)_a \rightleftharpoons (ML.HL)_o + (H^+)_a$$

$$K^{ex}_{ML.HL} = K_{ML}K^{(o)}_{ML.HL}K_aD_{ML}/D_{HL} = \frac{[(ML.HL)_o][(H^+)_a]}{[(HL)_o]^2[(M^+)_a]} \qquad (7)$$

The distribution ratio of metal ion, q_M, is then given by

$$q_M = \frac{[(ML)_o] + [(ML.HL)_o]}{[(M^+)_a] + [(ML)_a]} \simeq \frac{[(ML)_o] + [(ML.HL)_o]}{[(M^+)_a]} \qquad (8)$$

the concentration of the metal complex in the aqueous phase usually being negligibly small compared with that of the free metal ion. The quantity in the numerator in equation (8) is obtained experimentally by the relation,

$$[(ML.HL)_o] = \Delta A/\Delta\epsilon_{ML.HL} \qquad (9a)$$

or

$$[(ML)_o] = \Delta A/\Delta\epsilon_{ML} \qquad (9b)$$

where ΔA is the absorbance of the organic phase measured against the reagent blank (the organic phase when the alkali metal ion is not involved), and $\Delta\epsilon_{ML.HL}$ and $\Delta\epsilon_{ML}$ are the "apparent" molar absorptivities of the extracted species when the absorbance is measured against the reagent blank. $\Delta\epsilon_{ML.HL}$ and $\Delta\epsilon_{ML}$ are in fact taken as the differences in the molar absorptivities ($\epsilon_{ML.HL} - 2\epsilon_{HL}$) and ($\epsilon_{ML} - \epsilon_{HL}$), respectively, in the organic phase, and must be determined by a separate series of experiments. They are different from the values measured in the aqueous phase. In the absence of detailed structural information on the chromophoric interaction in the complex ML.HL, $\epsilon_{ML.HL}$ may be equated (to a first approximation) to the sum of ϵ_{ML} and ϵ_{HL}. In that case $\Delta\epsilon_{ML.HL}$ becomes equal to $\Delta\epsilon_{ML}$ ($=\Delta\epsilon$), and, thus, when both complexes are involved in the extraction,

$$[(ML)_o] + [(ML.HL)_o] = \Delta A/\Delta\epsilon \qquad (9c)$$

and

$$q_M = \frac{\Delta A/\Delta\epsilon}{[(M^+)_a]}. \qquad (10)$$

The concentration $[(M^+)_a]$ can be approximately equated, under ordinary conditions, to the concentration of the metal ion in the original aqueous solution, since in our conditions the amount of the metal ion transferred to the organic phase is small when compared with that remaining in the aqueous phase (about 2% for K^+, see below). By introduction of the extraction constants [equations (6) and (7)] into equation (8), another expression for q_M is derived:

$$q_M = \frac{K^{ex}_{ML}}{[(H^+)_a]}[(HL)_o] + \frac{K^{ex}_{ML.HL}}{[(H^+)_a]}[(HL)_o]^2. \qquad (11)$$

Equation (11) indicates that the slope of a plot of log q_M against log $[(HL)_o]$ at constant pH is either 1 or 2, depending on the stoichiometry of the extracted complexes. The $[(HL)_o]$ values for the plot are obtained from the total concentration of HL in the original organic solution, $[HL]_t$, after correction for the fraction converted into ML and ML.HL or

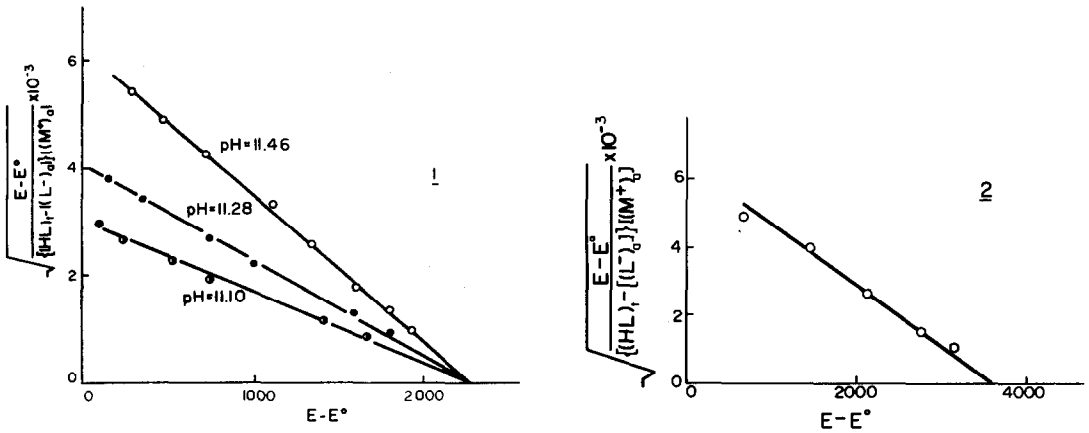


Fig. 2. Linear plot according to equation (15). Crown reagents **1** and **2**.

distributed into the aqueous phase [*vide infra*, *e.g.*, equation (13)].

Determination of $\Delta\epsilon$

In order to obtain the value of $\Delta\epsilon$, a modified Newton method[7] was used. In the case of extraction of potassium, the complex KL.HL is preferentially formed. If it is assumed that equal volumes of the organic and aqueous solutions are used and recalled that there is virtually no distribution of HL into aqueous phase, the following equations are obtained:

$$E = \frac{A}{[(HL)_o] + 2[(KL.HL)_o]} = \frac{A}{[HL]_t - [(L^-)_a] - [(HL)_a]} \simeq \frac{A}{[HL]_t - [(L^-)_a]} \quad (12)$$

$$[(HL)_o] = [HL]_t - 2[(KL.HL)_o] - [(L^-)_a] \quad (13)$$

$$[(KL.HL)_o] = \frac{(E - E^o)}{\Delta\epsilon}([HL]_t - [(L^-)_a]) \quad (14)$$

A stands for the absorbance of the organic phase measured against pure chloroform. E^0 is the value of E for the reagent blank and is equal to ϵ_{HL}. $[HL]_t$ represents the total (analytical) concentration of HL in the original chloroform solution. Combination of equations (7), (13) and (14) gives

$$\sqrt{\frac{E - E^o}{([HL]_t - [(L^-)_a])[(M^+)_a]}} = \sqrt{\frac{K^{ex}_{ML.HL}}{\Delta\epsilon[(H^+)_a]}}\{\Delta\epsilon - 2(E - E^o)\}. \quad (15)$$

Equation (15) means that, at constant pH, a plot of the quantity on the left-side of the equation against $(E - E^0)$ should be linear. Figure 2 verifies this expectation. In the calculation, $[(M^+)_a]$ was replaced by the metal concentration in the original aqueous solution, and $[(L^-)_a]$ for **1** was derived from the measured absorbance of the aqueous phase by using $\epsilon_{L^-(aqueous)} = 2.04 \times 10^4$ l.mole^{-1}.cm^{-1} at 445 nm. In the case of **2**, $[(L^-)_a]$ was found to be negligible. The intercepts with the co-ordinates of the plot at pH 11.46 gave $\Delta\epsilon$ (at 560 nm) $= 4.58 \times 10^3$ l.mole^{-1}.cm^{-1} and $K^{ex}_{KL.HL} = 10^{-7.55}$ for **1**. Similarly, the plot at pH 10.70 for **2** gave $\Delta\epsilon$ (at 550 nm) $= 7.57 \times 10^3$ l.mole^{-1}.cm^{-1} and $K^{ex}_{KL.HL} = 10^{-7.1}$. Plots at different pH values gave the same $\Delta\epsilon$ value, but the extraction constants were slightly different from one another (Table 1). The $\Delta\epsilon$ value obtained for K^+ was used in the calculation of the extraction constants for other metal ions. All of the approximations introduced in the treatments above proved to be self-consistent within the experimental error.

Extraction constants of alkali metal ions

The extraction constants for Na^+, K^+, Rb^+ and Cs^+ were obtained by plotting log q_M against log $[(HL)_0]$ according to equation (11). Such plots over the concentration range of $[(HL)_0]$ between 5×10^{-4} and $1.6 \times 10^{-3}M$ are shown in Figs. 3 and 4. All the slopes are quite close to 2.0 except in the case of Na^+ with **1**, where an upward curvature with varying slopes between 1 and 1.7 was obtained.[10] This indicates that K^+, Rb^+ and Cs^+ are extracted only as the complex ML.HL, while Na^+ is extracted as both ML and ML.HL. No extraction occurred with Li^+. The extraction constants evaluated are summarized in Table 2. It is obvious that the trend in magnitude of these constants reflects the compatibility between the hole-size of the crown-ether ligand and

Table 1. Effect of triethylamine concentration on $K^{ex}_{KL.HL}$

Concentration of triethylamine in chloroform, M	pH of aqueous solution	$pK^{ex}_{KL.HL}$
1.0	11.46	7.55
0.5	11.28	7.73
0.2	11.10	7.83
0.0	12.31	7.93

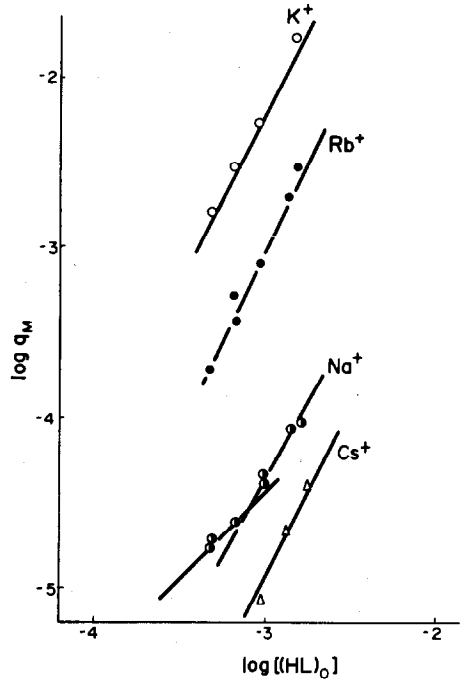


Fig. 3. Log q_M *vs.* log $[(HL)_0]$ according to equation (11). Crown reagent **1**.

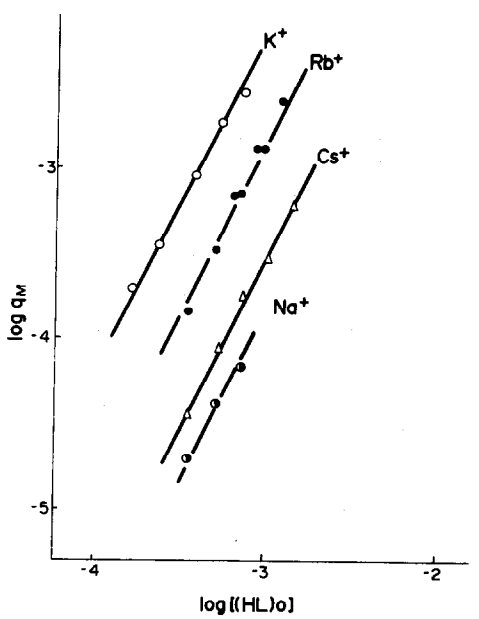


Fig. 4. Log q_M *vs.* log $[(HL)_0]$ according to equation (11). Crown reagent **2**.

the ionic radius of the incoming metal ion. Benzo-15-crown-5 forms a 1:2 (metal to ligand) complex of sandwich structure with K^+,[13,14] and it is probable that the complex ML.HL in the present study involves a similar structure. The order of extractability $K^+ > Rb^+ > Cs^+$ for both **1** and **2** also suggests that the extraction is not a simple ion-pairing mechanism as was the case for the extraction of alkali metal–dipicrylamine species into nitrobenzene, for which the reversed order, $K^+ < Rb^+ < Cs^+$, is reported.[15] The differences between the extraction constants of **1** and **2** with the same cation can be attributed to the difference both in pK_a of HL and in the distribution ratios of HL, ML.HL or ML. Since the pK_a of **2** is smaller than **1** by 1.8, and the distribution of HL into water is much smaller for **2**, the extraction of ML.HL should be much more efficient with **2** than with **1** (Table 2). The extraction constants in Table 2 indicate that **1** or **2** is a rather poor extraction reagent even for K^+. Thus, in our typical conditions (pH 11.46; $[(K^+)_a]$ $1 \times 10^{-2}M$; $[HL]_t$ $1.83 \times 10^{-3}M$; 25°) only 19% of the total amount of **1** employed is converted into ML.HL and extracted into chloroform. This is probably due to the large charge separation in the extracted complex. A reagent which allows the formation of tight ion-pair or chelate-type interaction between the anion and metal would improve the extraction. Alkaline earth metals could not be extracted with **1** or **2** under the conditions used in the present study. The properties of **3** were examined only briefly. The pK_a (9.32) falls between those of **1** and **2**, and the extraction behaviour is also intermediate between that of the other two.

Extraction solvent

Chloroform combined with triethylamine was used in the case of **1**. The primary aim of using triethylamine is to allow the dissociation of HL and assist the formation of the neutral complex ML or ML.HL. In this context, the selection of triethylamine was rather arbitrary, and the amine had to be used in fairly large amount to attain the required alkalinity (pH > 11). Thus, in our experimental practice, the pH values 11.46, 11.28 and 11.10 for the aqueous solution in equilibrium with chloroform were achieved only by employing 1.0, 0.5 and 0.2*M* triethylamine in chloroform, respectively. Since 0.2–1.0*M* triethylamine contains approximately 3–14% by volume of the amine, the nature of the extraction solvent may well be different from that of pure chloroform and depen-

Table 2. Extraction constants of alkali metal ions

Crown ether		Li^+	Na^+	K^+	Rb^+	Cs^+
1*	pK_{ML}^{ex}	—	~13	—	—	—
	$pK_{ML.HL}^{ex}$	—	~10	7.55	8.5	10.4
2†	$pK_{ML.HL}^{ex}$	—	~8.8	~7.1	~7.9	~8.3

* Water–chloroform (1.0*M* triethylamine).
† Water–chloroform (0.5*M* triethanolamine).

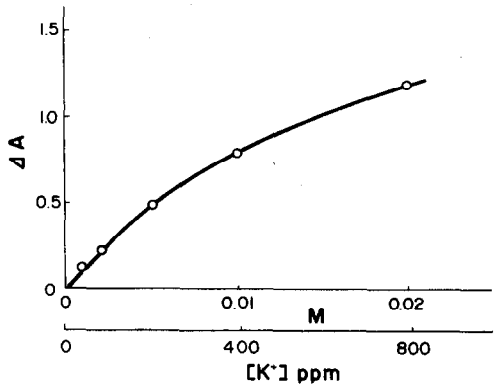


Fig. 5. Calibration curve for the colorimetric determination of K^+. Water–chloroform (1.0*M* triethylamine in chloroform), $[Na^+] = 0$–$10^{-2}M$.

dent on the concentration. Thus, the $K^{ex}_{KL,HL}$ value determined from the slopes of the plots in Fig. 2 decreases with decreasing concentrations of triethylamine in chloroform (Table 1). This indicates that the amine assists the extraction by acting both as base and co-solvent. In the extraction study of **2**, however, the triethylamine–chloroform solvent could not be used, because **2** dissociated in this solvent, even in the absence of metal ions in the aqueous phase. Thus, pure chloroform was used for **2**, and pH of the aqueous phase was adjusted to 10.70 by use of triethanolamine, which does not distribute into chloroform. The use of other solvents, *e.g.*, benzene, nitrobenzene or MIBK, proved less successful for both **1** and **2**.

Application to potassium determination

Rearrangement of equation (7) gives equation (16) which is convenient for analytical applications:

$$\frac{\Delta A}{(\alpha - \Delta A)^2} = \beta[(K^+)_a] \qquad (16)$$

where α and β stand for the experimental constants given by

$$\alpha = \frac{\Delta\epsilon}{2}\cdot([HL]_t - [(L^-)_a]) \simeq \frac{\Delta\epsilon}{2}\cdot[HL]_t \qquad (17)$$

and

$$\beta = \frac{4K^{ex}_{KL,HL}}{\Delta\epsilon[(H^+)_a]}. \qquad (18)$$

For the purpose of constructing a calibration graph according to equation (16), α may be calculated by using equation (17), while β is conveniently obtained experimentally with the aid of a series of standard solutions containing a known amount of potassium ion. A calibration graph according to equation (16) was found to be linear up to 800 ppm of K^+. At the low concentration of K^+ where ΔA is small compared with α, equation (16) reduces to a simple linear relationship between ΔA and $[(K^+)_a]$. The calibration graph thus obtained for **1** is shown in Fig. 5, and though there is strong curvature at high K^+ concentration, is valuable for practical purposes in the low concentration range below 100 ppm of K^+.

Though the extraction study suggests that most of

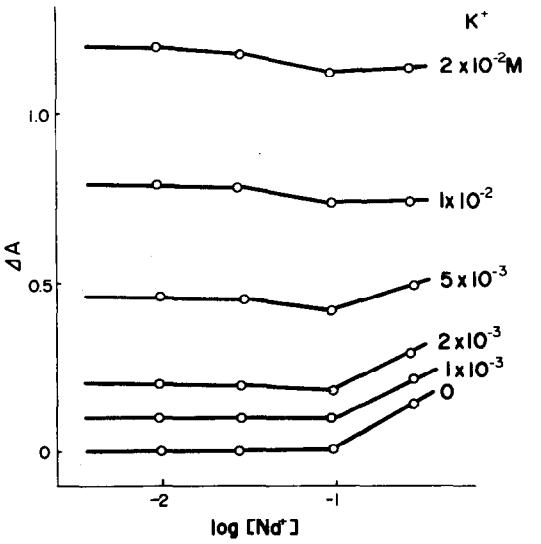


Fig. 6. Interference of Na^+ in the determination of K^+. Water–chloroform (1.0*M* triethylamine in chloroform).

the alkali and alkaline earth metals (except for Rb^+) do not interfere in the colorimetric determination of K^+ unless they are present in a large excess, this indication requires experimental support. The effect of Na^+ and Ca^{2+} on the determination of K^+ is illustrated in Figs. 6 and 7. The presence of Na^+ up to $3 \times 10^{-2}M$ concentration does not affect the measurement. Determination in presence of Na^+ above this limit is still possible, if necessary, with the aid of appropriate calibration curves constructed by use of standards containing specified amounts of sodium. No interference is observed with multivalent metal ions when they were properly masked with the lithium salt of EDTA. Use of EDTA dilithium salt, followed by the addition of lithium hydroxide to adjust the pH to 11.46, is recommended, since the use of the EDTA salt alone causes the pH to be lowered too far for restoration by triethylamine buffer. Of the interfering cations, calcium does not interact

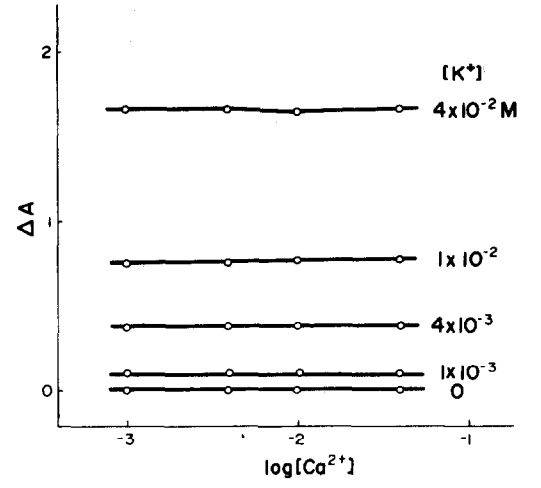


Fig. 7. Interference of Ca^{2+} in the determination of K^+. Water–chloroform (1.0*M* triethylamine in chloroform), Li–EDTA, pH = 11.46 ± 0.03.

Table 3. Determination of potassium in sea-water

Sample	Present method, *M*	Gravimetric analysis, *M*
A (Hakata Bay)	1.00×10^{-2}	0.998×10^{-2}
B (Nippon Sea near Fukuoka)	1.04×10^{-2}	1.038×10^{-2}

with **1**, and the masking itself is not an essential in the present method. However, the presence of 0.1–0.01*M* Ca^{2+} causes a considerable pH drop owing to hydrolysis of the metal ion under the proposed conditions. Readjustment of the pH by addition of lithium hydroxide allows the K^+ to be determined in the ordinary manner. On the other hand, the use of EDTA is indispensable when Mg^{2+} and other multivalent metal ions having insoluble hydroxides are present. Unless EDTA is employed, the extraction photometry cannot be used, because of extensive precipitation of the metal hydroxide.

In a practical application, potassium in sea-water was determined photometrically with the reagent **1**. The sea-water (2.5 ml) and 0.4*M* $(EDTA)_3Li_8$ salt solution (adjusted to pH 11.46, 2.5 ml) were shaken with a chloroform solution of **1** ($1.8 \times 10^{-3}M$, 5 ml) that was also 1*M* in triethylamine, and the absorbance of the organic phase was measured in the same way as in the extraction study of **1**. When the EDTA salt was not added, magnesium and calcium interfered seriously. The results in Table 3 verify the validity of the photometric analysis.

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AN INVESTIGATION OF A FLAMELESS ATOMIC-ABSORPTION METHOD FOR DETERMINATION OF ALUMINIUM, CALCIUM, IRON AND MAGNESIUM IN SEWAGE SLUDGE

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Summary—The methods currently used for the determination of aluminium, calcium, iron and magnesium in sewage sludge are time-consuming. A rapid flameless atomic-absorption procedure, utilizing homogenization of diluted samples as the only pretreatment, has been compared with wet and dry analytical methods followed by flame atomic-absorption analysis, in a statistically designed experiment. Low-sensitivity (secondary absorption) lines have been used for the flameless analysis. The flameless atomic-absorption method described is better than all the other methods tested, with the exception of the nitric–perchloric–hydrofluoric acid digestion procedure. The time saved is substantial and the method could be used advantageously for routine analysis.

One of the major problems confronting waste water treatment authorities today is the disposal of large volumes of sewage sludges. Because of cost and the environmental objections to some of the alternatives (incineration, landfill, disposal at sea), the disposal of liquid or dewatered sludges on land is common practice. In the United Kingdom it is estimated[1] that 80% of the sludges from all inland sewage treatment works are disposed of on land. Approximately half is applied to agricultural land; the value of its nutrient content has been demonstrated[2] and the organic matter present[2] may be valuable as a soil conditioner, though this has not been assessed quantitatively.

Because of the toxic nature of some of the elements present in sewage sludge, their concentrations must be determined before disposal, to ensure that the maximum concentrations permissible[2] are not exceeded.

Though not mentioned in current guidelines,[2] aluminium may be phytotoxic in acidic soils.[3] In addition, the need also exists to estimate the concentrations of certain plant nutrients such as calcium,[2] magnesium[2] and iron.[4] Iron deficiency has been encountered in calcareous soils but rarely arises in acidic soils.[5]

The concentrations of calcium and magnesium in sewage sludge may be up to five times greater than those typically found in soils;[6] the average aluminium concentration in sewage sludge is lower than that in soil and, generally, so is that of iron. The concentrations are likely to be high in sludges that are inorganically conditioned, in order to facilitate dewatering, with compounds such as ferrous sulphate (copperas), ferric chloride, lime or hydrated aluminium chloride (aluminium chlorohydrate) in dosages that can be as high as 30% of the total solid contents of sludges.[7]

A range of methods has been applied to the determination of these metals in waters, waste waters and sewage sludges; these include neutron-activation analysis,[8,9] X-ray fluorescence,[10] colorimetry[11] and atomic-absorption spectrophotometry.[12] Of these methods atomic-absorption spectrophotometry is probably the one most frequently employed for environmental samples.[13,14]

When applied to samples where organic and inorganic matrices are present, these methods generally require some form of pretreatment. Of the pretreatment methods available,[15,16] a limited number have achieved general use. Dry ashing is a common procedure for the destruction of organic matter[17,18] although low calcium results may occur if nitric acid dissolution is used.[18,19] Digestion with perchloric acid in conjunction with nitric acid is claimed to yield good recoveries,[14] but it is necessary to add hydrofluoric acid if aluminium is to be completely recovered from siliceous materials.[20] Procedures based on the use of sulphuric acid and nitric acid have been recommended for sludges[10] but some metals may be lost as insoluble sulphates.[16] Recently, methods using hydrogen peroxide and nitric acid have been successfully applied to environmental samples.[21,22]

The use of flameless atomizers allows sample pretreatment to be minimized for those samples with largely organic matrices.[13,23] Since flameless atomizers give better sensitivity than flame atomizers, low-sensitivity (secondary absorption) lines may be used when the concentration of the analyte is high, thus avoiding the need for excessive dilution.[24]

A rapid flameless atomic-absorption method has been used for the determination of cadmium, chromium, copper, lead, nickel and zinc in sewage sludges[25–27] and in sewages and effluents.[28] The results presented here have been obtained from a stat-

Table 1. Conditions for flame atomic-absorption analysis

Metal	Wavelength, nm	Spectral bandwidth, nm	Flame type	Working range, μg/ml
Al	309.3	0.7	Nitrous oxide–acetylene Reducing (rich, red)	1–50
Ca	422.7	0.7	Air–acetylene Oxidizing (lean, blue)	0.05–5.0
Fe	248.3	0.2	Air–acetylene Oxidizing (lean, blue)	0.05–5.0
Mg	285.2	0.7	Air–acetylene Oxidizing (lean, blue)	0.005–0.5

istically designed experiment to compare the rapid flameless method using low-sensitivity lines for the analysis of a homogenized sample, and the flame method using high-sensitivity lines for ashed and acid-digested samples. Three digestion procedures have been used, a sulphuric–nitric acid method, a nitric acid–hydrogen peroxide method and a nitric–perchloric–hydrofluoric acid method. An ashing procedure, using a temperature of 450°, has also been evaluated.

EXPERIMENTAL

Instrumental

A Perkin-Elmer model 603 atomic-absorption spectrophotometer equipped with deuterium background-correction was used for flame analysis. The conditions for analysis and the working ranges used are presented in Table 1. In order to remove interferences or suppress ionization, the samples and standards to be analysed for aluminium were made up to contain 2000 μg of potassium chloride per ml and those to be analysed for calcium and magnesium were made up to contain 0.5% w/v of lanthanum.[29]

The same spectrophotometer and a Perkin-Elmer HGA 76 heated-graphite atomizer were used for flameless analysis. The conditions and working ranges for flameless atomic-absorption analysis are presented in Table 2. The atomization programme consisted of drying at 100° for 30 sec, two-stage thermal decomposition with temperature increase from 100° to 400° in 45 sec (rate 2) followed by isothermal decomposition at 1200° for 30 sec and atomization at 2770° for 5 sec, for all metals except aluminium (8 sec). The first stage in the thermal decomposition avoided spattering of the sample which would have occurred if the temperature had been suddenly increased from 100° to 1200°.

Reagents

The hydrogen peroxide and the acids used were of "Aristar" quality.

Homogenization

Approximately 250 ml of the sludge sample, previously diluted fiftyfold and acidified with 1% of its volume of nitric acid, were homogenized in a 2-litre tall-form Pyrex beaker with an Ultra Turrax T45N homogenizer (Scientific Instrument Co. Ltd., London) for 5 min at 8000 rpm. Aliquots of 20 μl were injected into the flameless atomizer with an Eppendorf micropipette (Anderman & Co. Ltd., Surrey). Analysis was performed by direct comparison with standards prepared in 1% v/v nitric acid and checked by the method of standard additions.

Sulphuric–nitric acid digestion

Digestions were carried out as recommended.[11] The apparatus was modified slightly by the substitution of a 500-ml flask for the original 250-ml one, permitting larger samples (50 ml) to be treated. Heat was provided by an electric heating mantle.

To 50 ml of undiluted sludge in a 500-ml round-bottomed flask were added two glass anti-bumping granules (previously leached in 10% v/v nitric acid), 50 ml of conc. nitric acid and 20 ml of conc. sulphuric acid. The digestion was started at approximately 120° and when the volume was reduced to 10 ml the mixture was allowed to cool before addition of a further 20 ml of nitric acid. Successive 20-ml portions of nitric acid were added until white fumes were evolved and the solution was pale straw in colour. At this point the digestion was deemed complete. The mixture was allowed to cool and 10 ml of distilled water were carefully added. Insoluble matter was allowed to settle, and the solution was filtered through a Whatman GF/C glass-fibre filter (previously leached with 10% v/v nitric acid) into a 100-ml standard flask.

The 500-ml flasks were leached twice by boiling 15 ml of 10% v/v hydrochloric acid in them for 10 min, the acid and two distilled-water washes being added to the standard flask and the volume made up to 100 ml.

Nitric acid–hydrogen peroxide digestion

The method used was essentially that described.[21] However, 20 ml of sample were digested instead of the 5 ml originally proposed, thus reducing the errors involved in

Table 2. Conditions for flameless atomic-absorption analysis

Metal	Wavelength, nm	Spectral bandwidth, nm	Sample volume, μl	Working range, μg/ml
Al	257.5	0.2	20	0.20–4.0
Ca	239.9	0.7	20	1.00–20.0
Fe	305.9	0.2	20	0.20–5.0
Mg	202.6	0.7	20	0.02–0.50

the estimation of the volume of thick sludges. Digestions were done on a thermostatically controlled hot-plate.

To 20 ml of sample were added 30 ml of conc. nitric acid and two glass anti-bumping granules (previously leached overnight with 10% v/v nitric acid). When 30 ml had evaporated, a further 10 ml of acid were added and the digestion was continued until the volume was reduced to approximately 5 ml. At this point 2 ml of 100-vol. hydrogen peroxide and 2 ml of nitric acid were added, the addition being repeated until the solution was pale straw in colour.

The contents of the beaker were filtered into a 100-ml standard flask through a Whatman GF/C glass-fibre filter (previously leached with 10% v/v nitric acid). The beaker was then leached twice by boiling 15 ml of 10% v/v hydrochloric acid in it for 10 min. The acid and two distilled-water washes were added to the standard flask and the volume was made up to 100 ml.

Nitric–perchloric–hydrofluoric acid digestion

The method used was similar to that previously described,[30] with minor modifications. To 10 ml of sludge in a 100-ml PTFE beaker 30 ml of conc. nitric acid were added and the sample was evaporated nearly to dryness on a hot-plate. The beaker was cooled and 5 ml of conc. nitric acid, 2 ml of 60% perchloric acid and 6 ml of 40% hydrofluoric acid were added. The mixture was evaporated nearly to dryness on a hot-plate at a temperature not exceeding 280°. A further 2 ml of nitric acid and 2 ml of perchloric acid were added and evaporated to ensure that silicon and fluoride were removed. The beaker was cooled and 20 ml of 5% v/v nitric acid were added to dissolve the salts. The solution was transferred to a 100-ml standard flask, and made up to 100 ml with distilled-water washings from the digestion beaker.

Destruction of organic matter by ashing

Samples (25 ml) were placed in 100-ml Pyrex beakers which were then covered with porcelain crucibles to prevent contamination by clay dust from the firebrick lining of the muffle furnace. Initially the samples were charred at 200° for 1 hr, after which the temperature of the furnace was gradually increased over a period of 2 hr to 450°. Ashing was continued for 14 hr at this temperature. When it was completed, the beakers were removed and allowed to cool, after which 1 ml of conc. nitric acid was added to each and the residues were then heated to dryness on a hot-plate. The beakers were returned to the muffle furnace and the contents ashed at 450° for a further hour. The beakers were cooled, 10 ml of extraction acid were added to each (100 ml of conc. hydrochloric acid, 650 ml of distilled water and 150 ml of conc. nitric acid) and the contents heated almost at boiling point, on a hot-plate, for 10 min. The extracted samples were filtered through a Whatman GF/C glass-fibre filter (previously leached with 10% v/v nitric acid) into 100-ml standard flasks. The beakers were rinsed twice with 15 ml of distilled water, the washings added to the contents of the volumetric flasks and the volumes made up to 100 ml with distilled water.

RESULTS AND DISCUSSION

A sample of mixed primary sludge (total solids 3.04%) was collected in a polythene container that had twice been leached with 10% v/v nitric acid solution; the sample was acidified with 1% of its volume of nitric acid to keep metals in solution. For each pretreatment (digestion, ashing and homogenization) five replicates and two blanks were done. The ashed and digested samples were analysed by flame atomic-absorption spectrophotometry and the homogenized samples by flameless atomic-absorption spectrophotometry. The results obtained by flameless analysis were compared with results obtained by the standard-additions method and aqueous standard solutions and found to be in good agreement. The values reported are those obtained by direct comparison with aqueous standards.

The results were statistically treated; the mean values, within-group relative standard deviation and the results of an analysis of variance by the F-test[31] are reported in Table 3. Tukey's test[31] was used to identify which means were statistically different at the 0.05 significance level. The reproducibility of flameless analysis, based on ten injections of the same diluted sample, is indicated in Table 4.

No significant differences were found between the treatments in the determination of iron, but for the determination of aluminium, calcium and magnesium, highly significant differences were found between treatments. A comparison of the means by Tukey's test indicated that the sulphuric–nitric acid digestion procedure yielded lower results for calcium, but that there were no significant differences between the other pretreatments for this element.

For both aluminium and magnesium, Tukey's test indicated that no more than two of the pretreatments were in agreement for either element. It is perhaps significant that for both these elements the nitric–perchloric–hydrofluoric acid treatment in conjunction with flame atomic-absorption spectrophotometry, and homogenization in conjunction with flameless atomic-absorption spectrophotometry, are in agreement. Moreover these two treatments also yielded the highest recoveries for these two elements. It would be expected that the nitric–perchloric–hydrofluoric acid digestion procedure would give complete recovery, which further substantiates the suitability of the flameless atomic-absorption method for the determination of total concentrations of aluminium and magnesium.

For the analysis of lake sediments it has been reported[14] that a nitric–perchloric–hydrofluoric acid digestion method extracts slightly more calcium and magnesium and considerably more aluminium and iron than other digestion procedures similar to those employed in the work reported here. This is consistent with the results presented for aluminium and magnesium, but not for calcium and iron. For calcium only the nitric–sulphuric acid digestion method yielded low recoveries, which is probably a result of the formation of slightly insoluble calcium sulphate. All digestions performed equally well for iron, which might be a result of the absence of mineralized iron in this sample.

It has been reported that dry-ashing procedures give almost complete recovery of iron[17,18] and magnesium,[18] but low results for calcium were observed when a hydrochloric–nitric acid recovery was employed. Problems associated with the preparation of botanical samples to be analysed for calcium have

Table 3. Comparison of aluminium, calcium, iron and magnesium concentrations in sewage sludges, found by using sulphuric–nitric acid digestion, hydrogen peroxide–nitric acid digestion, perchloric–nitric–hydrofluoric acid digestion, and ashing at 450°C followed by flame atomic-absorption analysis, with those found for homogenized samples analysed by flameless atomic-absorption analysis

Metal	Pretreatment	Analytical method	*F*-test level of significance	Mean conc. μg/ml	RSD %
Al	H_2SO_4–HNO_3	F	0.01	140a*	6.2
	H_2O_2–HNO_3	F		120ac	6.4
	$HClO_4$–HF–HNO_3	F		223b	4.7
	Ashing (450°)	F		107c	4.0
	Homogenization	FL		230b	7.8
Ca	H_2SO_4–HNO_3	F	0.01	764a	3.2
	H_2O_2–HNO_3	F		838b	2.3
	$HClO_4$–HF–HNO_3	F		828b	2.0
	Ashing (450°)	F		854b	2.4
	Homogenization	FL		836b	2.0
Fe	H_2SO_4–HNO_3	F	NS	113a	3.1
	H_2O_2–HNO_3	F		110a	5.7
	$HClO_4$–HF–HNO_3	F		113a	3.7
	Ashing (450°)	F		108a	4.1
	Homogenization	FL		111a	3.1
Mg	H_2SO_4–HNO_3	F	0.01	71ac	3.3
	H_2O_2–HNO_3	F		71a	2.1
	$HClO_4$–HF–HNO_3	F		83b	2.3
	Ashing (450°)	F		67c	2.7
	Homogenization	FL		82b	2.3

* = means having a common following letter are not significantly different at the 0.05 probability level.
NS = not significant at the 0.05 probability level.
RSD = relative standard deviation.
F = flame analysis.
FL = flameless analysis.
H_2SO_4–HNO_3 = sulphuric–nitric acid digestion.
H_2O_2–HNO_3 = hydrogen peroxide–nitric acid digestion.
$HClO_4$–HF–HNO_3 = perchloric–hydrofluoric–nitric acid digestion.
Ashing (450°c) = ashing at 450°C for 16 hr followed by dissolution.
Homogenization = pretreatment by homogenization.

been investigated[19] and show that the recovery of calcium from ashed samples can be almost complete, which agrees with the results reported here. The low recoveries for aluminium and magnesium could be due to the formation of insoluble materials that would require fusion with sodium carbonate[32,33] if complete recovery were to be achieved, so incomplete dissolution could have taken place. For magnesium, another possible cause of error may have been the temperature used for ashing; in the analysis of shrimp tissue, an increase in recovery of approximately 20% was achieved by increasing the ashing temperature from 460° to between 535° and 620°.[34]

Table 4. Reproducibility of flameless analysis of diluted sewage sludge samples (10 injections)

Metal		Concentration, μg/ml Mean	SD	RSD, %
Al	best*	2.2	0.13	5.9
	worst	2.3	0.25	10.8
Ca		16.6	0.29	1.7
Fe		2.28	0.06	2.6
Mg		0.415	0.008	1.9

* See text.

The homogenization procedure coupled with flameless atomic-absorption analysis and direct comparison with aqueous standards has proved to be a suitable method for the determination of aluminium, calcium, iron and magnesium in sewage sludges. This dispenses with the need for drastic pretreatments such as the nitric–perchloric–hydrofluoric acid digestion procedure and also the need to add different interference-removal agents to permit analysis by flame atomic-absorption spectrophotometry.

For aluminium, the precision of the results varied with the time of day at which they were obtained. The relative standard deviation of ten injections for a sample of approximately 1.0 μg/ml concentration varied from 6% to approximately 11% (Table 4). This could have been due to variations in voltage that resulted in slight temperature variations in the furnace at the time of atomization, yielding different results. Reported values for the flameless analysis of

biological samples quote relative standard deviations of 8% for the determination of aluminium in whole blood[35] at the 0.4-μg/ml level and 10% for biological tissue[23] (approximately 1 μg/ml). Deuterium background-correction was not required for the determination of aluminium.

The use of low-sensitivity lines for the determination of calcium and magnesium by flameless atomic-absorption spectrophotometry substantially reduces the amount of dilution that would be needed and so the amount of contamination which might occur if very sensitive lines were used. The analysis is simple and there is no need to use deuterium background-correction, which agrees with previously reported results.[36]

Determination of iron by flameless atomic-absorption yielded reproducible results, did not require the use of deuterium background-correction, and the use of low-sensitivity lines substantially reduced the dilution required. Non-sensitive lines have been used previously with similar results for blood serum,[37] soils and sediments.[24]

CONCLUSION

The rapid flameless procedure described here can be used advantageously for routine analysis. The time saved is considerable since homogenization takes only 5 min as opposed to 3–6 hr for digestion or approximately one day for ashing. This more than compensates for the additional time (2–3 min) required for flameless analysis as opposed to flame analysis. The method has a further advantage over flame atomic-absorption in that it does not require interference-removal agents to be added to samples and standards before analysis.

This method, based as it is on the analysis of a single, albeit typical, sewage sludge, should be evaluated against the nitric–perchloric–hydrofluoric acid digestion procedure followed by flame analysis, for a range of such materials before it can be applied as a routine method in sewage treatment works.

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SPECTROPHOTOMETRIC DETERMINATION OF MICRO AMOUNTS OF MOLYBDENUM AND VANADIUM BY REDUCTION OF IRON(III) IN THE PRESENCE OF FERROZINE

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Summary—Molybdenum and vanadium, in the range 0.1–1 ppm, have been determined with a relative precision of 1–2% with iron(III) in the presence of Ferrozine. The separation of molybdenum and vanadium from interfering elements has been achieved by ion-exchange with either cation-exchange RG 50 followed by anion exchanger AG 1-X8, or the exchange-resin NBL 17.

Micro amounts of molybdenum are commonly determined spectrophotometrically by the thiocyanate–stannous chloride,[1,2] xanthate,[3] and other colorimetric methods.[4–10] In many of these methods molybdenum(VI) is reduced in acid medium; it is then complexed, concentrated by extraction or ion-exchange, and finally determined colorimetrically by the peroxide,[11] phosphovanadotungstic acid[12] and other spectrophotometric methods.[13–16]

An indirect method for the determination of molybdenum and vanadium has been developed and is described in this note; iron(III) is used in the presence of Ferrozine, which forms a complex with the iron(II) produced by reduction with molybdenum(III) or vanadium(II) in acid solution. In this manner, concentrations as low as 0.15 ppm have been determined by measuring the absorbance of $Fe(II)(Ferz)_3^{4-}$ at 562 nm. Molybdenum and vanadium have been separated from many other cations by use of cation- and anion-exchange resins, or Poly Cycle NBL 17 special resin.

EXPERIMENTAL

Reagents

All reagents were of reagent grade, and were used without further purification. Demineralized water was used to prepare all the solutions. Stock solutions of molybdenum(VI) and vanadium(V) were prepared by dissolving weighed amounts of pure ammonium molybdate and ammonium metavanadate, and analysed by the redox method.[17] Five-ml aliquots of the standardized molybdenum(VI) and vanadium(V) solutions were added to 60 ml of concentrated hydrochloric acid and diluted accurately to 500 ml. The solutions were stored in Teflon bottles and suitable aliquots were used for analyses.

A 0.003*M* iron(III) solution was prepared by dissolving 0.7233 g of ferric ammonium sulphate 12-hydrate in about 100 ml of water plus 3 ml of concentrated perchloric acid and 1 ml of concentrated nitric acid. The solution was heated until perchloric acid fumes appeared, cooled and diluted to 500 ml.

Ferrozine, 3-(2-pyridyl)-5,6-bis(4-phenylsulphonic acid)-1,2,4-triazine monosodium salt monohydrate, was purchased from Hach Chemical Co., Ames, Iowa. A 0.012*M* stock solution was prepared by dissolving 0.6125 g of it in 100 ml of water. Concentrated hydrochloric, perchloric and hydrobromic acids were used to prepare dilute acid solutions for elution purposes. A 1% ammonium hydrogen fluoride solution and 0.1*M* sodium chloride were prepared by dissolving weighed amounts of each salt in 100 ml of water. Sodium bicarbonate was used to neutralize free acid, and 0.3*M* pH-3.5 monochloroacetate buffer was used to achieve the optimum pH. The zinc amalgam for the Jones reductor was prepared by the conventional methods.

AG 1-X8, 100–200 mesh, anion-exchange resin was purchased from BioRad Chemicals; the NBL-17 resin was purchased from Poly Cycle, Inc., Palo Alto, Ca., and the RG 50 (H^+-form) cation-exchanger was purchased from Fisher Scientific Company.

Procedure

Determination of molybdenum and vanadium alone. Suitable amounts of molybdenum(VI) and vanadium(V) stock solutions, which had been adjusted to have a hydrochloric acid concentration of about 1.44*M*, were passed through a Jones reductor, which was made by filling a 5-ml volume of a 30-ml burette with 20-mesh amalgamated zinc. Before each use, the reductor was washed with water and 12% hydrochloric acid. The hydrochloric acid concentration was kept in the range 1.36–1.55*M* for all samples and wash solutions. The tip of the reductor was inserted into one of two holes in a rubber stopper in the top of an 80-ml beaker, wrapped in aluminium foil to prevent direct exposure to light. Two ml of 0.003*M* iron(III) were added through the other hole and the solution was then purged with nitrogen gas. Molybdenum(VI) was then allowed to pass through the Jones reductor into the beaker at a rate of one drop every 2 sec. The reductor was then washed three times with approximately 1.44*M* hydrochloric acid so as to bring the total volume in the beaker to approximately 19 ml. The nitrogen was turned off, and 2 ml of 0.012*M* Ferrozine were added. Sodium bicarbonate powder was then added slowly to bring the pH to 3.5, followed by addition of 10 ml of chloroacetate buffer, pH 3.5. The solution was then transferred into a 50-ml volumetric flask, 1 ml of 1% ammonium hydrogen fluoride solution was added, and the solution was diluted to volume. The absorbance of the complex was measured at 562 nm, in a 1-cm cell. Vanadium was determined in the

same way, but after the adjustment of the pH, the solution was allowed to stand for 20 min before the addition of the fluoride solution. The reaction of vanadium(II) with iron(III) is slower than that of molybdenum(III).

Determination of molybdenum in mixtures. Mixtures containing Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, molybdenum(VI) and vanadium(V) in 0.1*M* hydrochloric acid were made by taking suitable aliquots of various stock solutions.

Molybdenum(VI) and vanadium(V) were separated from the other ions by using either a combination of cation- and anion-exchange resins when the amount of cations was not too large relative to that of the molybdenum and vanadium, or by using the NBL 17 resin. The cation-exchange resin was first conditioned with 0.1*M* hydrochloric acid, then a suitable aliquot of the mixture was passed through it (2 cm bed length, 0.5 cm diameter) and the ions were eluted with 17 ml of 0.1*M* hydrochloric acid, followed by 13 ml of 0.1*M* sodium chloride. The eluate, containing only molybdenum(VI) and vanadium(V), was collected and evaporated to 5 ml, and the acidity was adjusted to 6*M* with hydrochloric acid. The solution was then placed on the anion-exchanger, AG 1-X8, 200 mesh, (2 cm bed length, 0.5 cm diameter) which had been equilibrated with 6*M* hydrochloric acid. Vanadium(V) was eluted with 10 ml of 6*M* hydrochloric acid. The acidity of the eluate was adjusted to approximately 1.44*M* with concentrated sodium hydroxide solution, and the solution was then passed through the Jones reductor and washed with 15 ml of 12% hydrochloric acid into iron(III) solution purged with nitrogen; the procedure followed was then the same as that for vanadium alone. The molybdenum(VI) remaining in the anion-exchanger was eluted with 13 ml of 0.5*M* hydrochloric acid. The acidity of the eluate was adjusted to about 12% hydrochloric acid by addition of the concentrated acid and the solution was treated in the same manner as for molybdenum alone.

The highly selective NBL 17 resin was used to separate molybdenum from other cations present in high concentrations. The resin was conditioned with concentrated hydrobromic acid and washed with 10 ml of distilled water and 5 ml of 0.01*M* hydrochloric acid. Then a suitable aliquot containing high concentrations of Fe^{3+}, Fe^{2+}, Cr^{3+}, Cu^{2+} and Ni^{2+} together with small amounts of molybdenum(VI) and vanadium(IV) was passed through the NBL 17 resin (2.0 cm bed length, 0.5 cm diameter) at the rate of one drop in 3 sec. The resin was washed with 3 ml of 0.01*M* hydrochloric acid followed by 15 ml of demineralized water. Molybdenum(VI) was eluted with 10 ml of 1.0*M* hydrobromic acid at the rate of one drop every 4 sec. The acidity of the eluate was adjusted to about 1.44*M* with concentrated hydrochloric acid, yielding a solution ~0.9*M* in hydrobromic acid and ~0.54*M* in hydrochloric acid. This solution was then passed through the Jones reductor, preconditioned and washed with 12% hydrochloric acid, into deaerated iron(III) solution. The resulting solution was then treated in the same manner as for molybdenum alone.

The molybdenum(VI) was also eluted from the NBL 17 resin with 1 ml of 8*M* perchloric acid followed by 11 ml of 2*M* perchloric acid. The acidity was then adjusted to 2*M* with demineralized water and the solution passed through the Jones reductor. After neutralization of the acid, the colour developed slowly and the absorbance was measured after 30 min.

The NBS-15-F steel sample was analysed for molybdenum by dissolving a weighed amount of steel in hydrochloric–nitric acid mixture (5:1). The solution was heated until most of the nitric acid was evaporated. Then a few crystals of ammonium ferrous sulphate were added to reduce vanadium(V) to vanadium(IV). The excess of acid was evaporated, the pH was adjusted to approximately 1.5–2.0, and the solution was then passed through the NBL 17 resin, leaving the molybdenum(VI) on the resin. The molybdenum was then eluted with 1.0*M* hydrobromic acid, and after adjustment of the acidity with hydrochloric acid to about 1.44*M*, the solution was passed through the Jones reductor into deaerated iron(III) solution as in the procedure described previously.

In all cases, the blanks were prepared in identical manner to the samples, except that the aliquots contained no molybdenum. The absorbance was read against water and then corrected for the blank.

RESULTS AND DISCUSSION

The determination of molybdenum and vanadium is achieved indirectly. First, both are reduced by the Jones reductor as follows:

$$\mathrm{Mo(VI) + V(V) \xrightarrow[\mathrm{Zn(Hg)}]{2M\ HClO_4,\ 1.44M\ HCl\ or\ 0.94M\ HBr + 0.50M\ HCl} Mo(III) + V(II)}$$

Secondly, molybdenum(III) and vanadium(II) in acid media and in the absence of oxygen are oxidized by iron(III):

$$\mathrm{Mo(III) + 4H_2O + 3Fe(III) \xrightarrow[\text{mod. fast in } 1.44M\ HCl \text{ and HBr}]{\text{slow in } 2M\ HClO_4} MoO_4^{2-} + 3Fe(II) + 8H^+}$$

and

$$\mathrm{V(II) + H_2O + 2Fe(III) \xrightarrow{\text{slow in both acids}} VO^{2+} + 2Fe(II) + 2H^+}$$

Finally, the liberated iron(II) is chelated with Ferrozine in the pH range 3.2–4.0:

$$\mathrm{Fe(II) + 3Ferz^{2-} \xrightarrow[\text{fast}]{\text{pH 3.2–4.0}} Fe(II)(Ferz)_3^{4-}.}$$

Since the molar absorptivity for $Fe(II)(Ferz)_3^{4-}$ at 562 nm is 2.8×10^4 $l.mole^{-1}.cm^{-1}$, the apparent molar absorptivities expected for molybdenum and vanadium are 8.40×10^4 and 5.60×10^4 $l.mole^{-1}.cm^{-1}$ respectively; the values found were 8.37×10^4 and 5.46×10^4 respectively (Table 1).

In carrying out these reactions, some precautions should be taken.

1. The amalgamated zinc in the Jones reductor should be kept under water and the reductor should be flushed with dilute acid before use.

2. The acidity of the solutions before the passage through the Jones reductor should be within the range 1.36–1.51*M* hydrochloric acid. Otherwise the reduction is incomplete.

3. Molybdenum and vanadium solutions should be passed through the reductor at a slow rate, one drop every 2 sec, otherwise the reduction may be incomplete.

4. The iron(III) solution used to collect the effluent from the Jones reductor should be purged with nitrogen to prevent oxidation of molybdenum(III) and vanadium(II) with dissolved oxygen.

5. The resulting acid solution should be cautiously

Table 1. Absorbance as a function of molybdenum and vanadium concentrations

Element	Amount, *ppm*	Absorbance*	Absorptivity, $l.mole^{-1}.cm^{-1}$
Mo(VI)	0.095	0.082	8.28×10^4
	0.190	0.166	8.38×10^4
	0.474	0.414	8.38×10^4
	0.948	0.834	8.44×10^4 $\epsilon_{app} = (8.37 \pm 0.07) \times 10^4$
V(V)	0.078	0.082	5.36×10^4
	0.157	0.170	5.52×10^4
	0.236	0.259	5.59×10^4
	0.471	0.487	5.27×10^4
	0.785	0.859	5.57×10^4 $\epsilon_{app} = (5.46 \pm 0.10) \times 10^4$

* Based on 5 independent measurements and corrected for the blank absorbance. The absorbance is measured at 562 nm, pH 3.2.

	Molybdenum	*Vanadium*
Correlation coefficient	0.9999	0.9992
Slope	0.877	1.087
Intercept	−0.002	−0.004

neutralized with powdered sodium bicarbonate; otherwise some of the solution may be lost as spray in the evolution of carbon dioxide.

6. The reaction time allowed for iron(III) with molybdenum(III) and vanadium(II) in perchloric acid must be about 30 min, but in 1.44*M* hydrochloric + hydrobromic acid it can be less than 10 min. Chloride and bromide apparently catalyse the reaction.

Interference of cations such as iron(II) and (III), cobalt(II), chromium (III) or (VI) is serious, and thus these ions must be removed before passage of the solutions through the Jones reductor. The separation is achieved either by the cation-exchanger[18] followed by the anion-exchanger[19] or by the special NBL 17 resin alone.[20] In the first case, after the passage through the cation-exchanger, vanadium(V) is separated from molybdenum(VI) by an anion-exchanger in 6*M* hydrochloric acid medium. In this manner, molybdenum(VI) is retained and is then eluted by changing the hydrochloric acid concentration to 0.5*M*. Elution patterns for molybdenum(VI) and vanadium(V) from the anion-exchange resin AG 1-X8 and the special resin NBL 17 are shown in Figs. 1 and 2.

When using the cation-exchange resin it is necessary to ensure that the vanadium(V) is eluted as VO_2^+ or $V(OH)_4^+$ with 0.1*M* sodium chloride.

The results for the analyses of mixtures containing various cations, vanadium(V) and molybdenum(VI), as well as the results of the analyses of the NBS-F-15 steel samples, are summarized in Table 2. With the cation- and an ion-exchange resins used in combination with hydrochloric acid, the experimental results

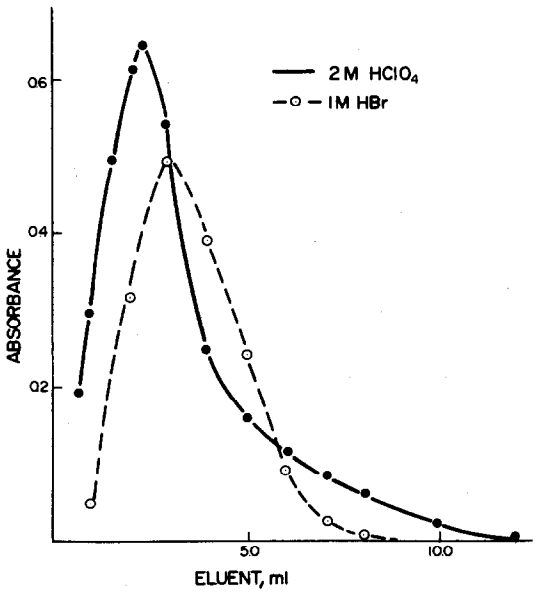

Fig. 1. Elution profiles for molybdenum(VI) and vanadium(V) from the AG 1-X8 resin with 6.0*M* HCl for V(V) and 0.5*M* HCl for Mo(VI).

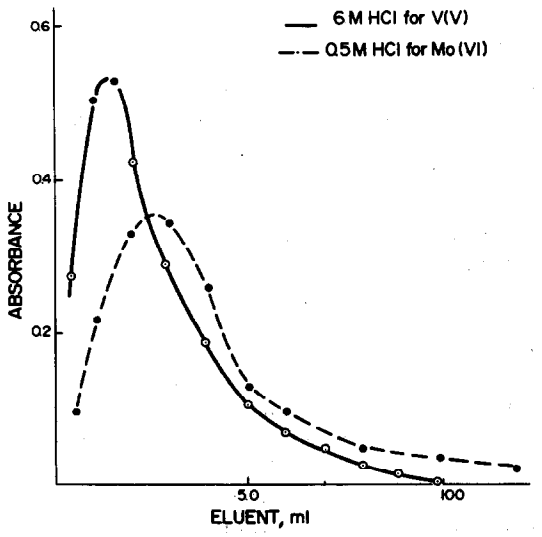

Fig. 2. Elution profiles for molybdenum(VI) from the NBL 17 resin with 1*M* HBr and 2*M* $HClO_4$.

Table 2. Summary of results for the determination of molybdenum

Sample/Mixture*	Type of resin	Eluent	Ion	Total amount taken, μg,	Found, μg†§	Net absorbance, $\bar{A}$
A	Cation, RG-50	0.1*M* HCl 0.1*M* NaCl	V			
	Anion, AG-1-X8	6*M* HCl	V	31.0	30.3 ± 0.1	0.333
		0.5*M* HCl	Mo	34.0	33.4 ± 0.1	0.292
B	Cation, RG-50	0.1*M* HCl 0.1*M* NaCl	V	31.0	30.4 ± 0.1	0.334
	Anion, Ag-1-X8	6.0*M* HCl 0.5*M* HCl	Mo	49.0	49.6 ± 0.1	0.434
C	NBL-17	8*M* and 2*M* $HClO_4$	Mo	48.0	46.5 ± 0.2	0.407
D	NBL-17	8*M* and 2*M* $HClO_4$	Mo	38.4	37.2 ± 0.2	0.326
E	NBL-17	1*M* HBr	Mo	41.1	41.5	0.363
F	NBL-17	1*M* HBr	Mo	24.6	23.9	0.209
G	NBL-17	1*M* HBr	Mo	57.5	57.3	0.502
NBS-15-F	NBL-17	1*M* HBr	Mo	21.0	20.4	0.178
NBS-15-F	NBL-17	2*M* $HClO_4$	Mo	18.0	18.5	0.161

* Composition of mixtures, $\mu g/100\ ml$

Mixture	Mo(VI)	V(V)	Fe(III)	Fe(II)	Mn(II)	Co(II)	Cr(III)	Ni(II)	Cu(II)
A	34.0	31.0	22	—	17	—	31	41	—
B	49.0	31.0	17	—	—	—	—	29	—
C	48.0	51.0	112	559	—	118	104	117	127
D	38.4	41.0	101	449	—	106	94	105	114
E	41.1	25.5	—	6000	—	118	104	—	127
F	24.6	30.6	112	6000	—	59	—	117	127
G	57.5	15.3	112	4000	—	—	156	—	64

† Amount of molybdenum found per 100 ml of solution.
§ Statistical data

Eluent	HCl		HBr	$HClO_4$
Element	V	Mo	Mo	Mo
Correlation coefficient	0.9999	0.9996	0.9996	0.9999
Slope	0.9591	0.8794	0.8906	0.8406
Intercept	0.0362	−0.003	0.085	0.003

for the molybdenum and vanadium are in good agreement with the theoretical values for those mixtures containing iron, chromium, and other cations in no greater amount than 10–20 times that of molybdenum or vanadium (it is important not to overload the cation-exchanger). These results are determined with a relative precision better than 1% for the solutions containing 1 ppm of molybdenum or vanadium in the solutions measured. In hydrochloric acid or in hydrochloric–hydrobromic acid mixture the reaction of iron(III) with molybdenum(III) is moderately fast, while the reaction of vanadium(II) is slow and the colour is not readily developed. In perchloric acid medium, molybdenum(III) as well as vanadium(II) reacts slowly with iron(III).

The NBL 17 resin retains molybdenum(VI), vanadium(V) and tungsten(VI) quantitatively at pH 1.5–2.0 (0.01*M* acid solution) while cations such as iron(II), iron(III), cobalt(II), chromium(III), copper(II), vanadium(VI) are not retained by the resin. Vanadium(V) is reduced by the addition of iron(II) before passage of the solutions through the resin. The VO^{2+} produced is not retained by the NBL 17 resin. Once the molybdenum(VI) is sorbed on the NBL 17 resin it must be eluted immediately, otherwise some of the molybdenum(VI) interacts with the resin on standing and is not readily eluted. Tungsten(VI) behaves like molybdenum in all respects and interferes seriously. The Mo(VI) is eluted from the NBL 17 resin with 1*M* hydrobromic rather than 2*M* perchloric acid since doing so cuts down the amount of acid used and the time needed for colour development. Furthermore, the relative precision for the determination of molybdenum at the 1-ppm level in perchloric acid is approximately 2% while in hydrobromic–hydrochloric acid mixture it is 1%.

After the elution of molybdenum(VI) with hydrobromic acid and before the passage through the Jones

reductor, the acidity is adjusted to approximately 1.44*M* with hydrochloric acid rather than with hydrobromic acid, as this gives lower blank values.

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ADSORPTION OF MERCURY(II) ON MACRORETICULAR STYRENE–DIVINYLBENZENE COPOLYMER BEADS

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Summary—The adsorption characteristics of mercury(II) on several kinds of styrene–divinylbenzene copolymer beads having different surface properties were studied. It was found that the polymer beads selectively adsorbed mercury(II) from solutions over a wide range of pH with high efficiency. The amount of mercury(II) adsorbed increased with increase in specific surface area of the polymer beads and the adsorption behaviour was found to be of the Langmuir type. The presence of chloride strongly reduced the adsorption, but this interference was not observed with nitrate, sulphate, perchlorate, cadmium(II), cobalt(II), copper(II), nickel(II), silver(I) and zinc(II). More than 95% of the mercury(II) adsorbed on a column of polymer beads could be recovered with dilute hydrochloric acid.

Macroreticular (MR) styrene–divinylbenzene copolymers, such as Amberlite XAD-2 and -4, have been widely used as adsorbents for a variety of organic substances. However, little is known of their adsorption of metal ions, except in the presence of chelating agents.[1–3] Previously, we have suggested that physical sorption, as well as chelate formation, contributes to mercury uptake on MR-type chelating resins containing oxine and thioureido groups.[4]

This paper deals with the adsorption of mercury(II) on several kinds of MR polymer beads prepared by the copolymerization of styrene and divinylbenzene. The applicability of these polymer beads to separation and concentration of mercury(II) is discussed. The adsorption and desorption behaviour of mercury(II) is compared with that observed for Amberlite XAD-2 and -4.

EXPERIMENTAL

Materials and reagents

Styrene (or ethylstyrene)–divinylbenzene (DVB) copolymer beads (MR-7.5, -15, -30 and -50) were prepared by the method reported previously.[5] Gel-type copolymer (Gel-50) was prepared by the copolymerization of commercial DVB solution (about 50–55%) which had been pretreated to remove stabilizer. A fraction, 35–60 mesh, of the polymer beads was collected. The commercially available Amberlite XAD-2 and -4 were also used after washing with large amounts of methanol. Beads, fully swollen in 30% ethanol, were used in adsorption studies of metal ions.

The stock metal ion solutions, approximately 0.1*M*, were prepared by dissolving reagent grade nitrates or chlorides in water and standardized by titration with EDTA. The solutions used for adsorption studies were prepared by diluting aliquots of the stock solutions with the desired background acid or buffer solutions (0.2*M* acetic acid–0.2*M* sodium acetate).

The radioisotopes, ^{60}Co, ^{65}Zn, ^{109}Cd, ^{110m}Ag and ^{203}Hg, as chlorides or nitrates, were supplied by the New England Nuclear Corp. and the Radiochemical Centre and were used as tracers.

Adsorption of metal ions by batch operation

Aliquots (10–50 ml) of aqueous metal ion solutions (0.1–0.001*M*) were shaken with weighed amounts of the swollen polymer beads (100 mg of dry beads) for a selected time, with a mechanical shaker. The amount of each metal ion adsorbed on the polymer beads was determined by measurement of the gamma-activity of equal portions of the solution, before and after the adsorption of metal ions. Nickel and copper were determined by titration with EDTA.

Column operation

A glass column (length 30 cm, bore 10 mm) was filled with swollen polymer beads (4 g of dry beads). The bed-volumes for the MR-50 and XAD-4 columns were 12.9 and 11.8 ml, respectively. The column was washed with 50 bed-volumes of buffer or acid solutions. The sample mercury(II) solution was passed through the column at a flow-rate of 1 ml/min. The column was then washed with 10 bed-volumes of the buffer or acid solutions used for conditioning. The mercury(II) retained was eluted with hydrochloric acid and determined as described above.

Adsorption isotherms

A flask containing the swollen MR-50 or XAD-4 (2–200 mg of dry beads) and 100 ml of $1 \times 10^{-4}M$ mercuric nitrate (in 0.2*M* acetic acid–0.2*M* sodium acetate, pH 5.0) containing the radioactive tracer (^{203}Hg) was shaken at 20° for 24 hr. After the shaking, the radioactivity of the filtrate was measured.

RESULTS AND DISCUSSION

The surface properties of the polymer beads used in this study are listed in Table 1. In the MR-series of beads, the specific surface areas increase with the amount of cross-linking. In a preliminary experiment, it was found that mercury(II) was strongly adsorbed over a wide pH range on those polymer beads having a large surface area. However, these beads show no affinity for other metal ions such as cadmium, cobalt(II), copper(II), nickel, silver and zinc.

Table 2 summarizes the adsorption behaviour of mercury(II) on the polymer beads. The efficiency of

Table 1. Physical properties of polymer beads

Polymer beads	DVB content of monomer,* %	Specific surface area, m^2/g	Pore volume, cm^3/g	Average pore diameter, nm
G-50	50	0	0	—
MR-7.5	7.5	19	0.43	90.5
MR-15	15	61	1.22	80.0
MR-30	30	149	1.32	35.0
MR-50	50	378	1.44	15.0
XAD-2[12]	—	300	0.69	9.0
XAD-4[12]	—	784	1.00	5.0

* The commercial DVB solution was regarded as having 50% DVB content.

adsorption of mercury(II) is affected by the physical properties of the beads, the amount adsorbed increasing with increase of surface area. MR-50 XAD-2 and XAD-4 show a strong affinity for mercury(II) even in strongly acidic solutions.

The rate of adsorption of mercury(II) was determined by batch operation with MR-50 and XAD-5. Figure 1 illustrates the experimental results, indicating that the adsorption from a buffer solution of pH 5.0 is rapid. Most of the mercury(II) is adsorbed in 1 hr. However, the rate of adsorption of mercury(II) from 0.01*M* nitric acid medium is relatively slow, and this feature was particularly marked for XAD-4.

It can be seen from Fig. 2 that the adsorption behaviour of mercury(II) is of the Langmuir type.[6] The capacity of MR-50 and XAD-4 for mercury(II) (q_∞) at pH 5.0 was calculated by using the Langmuir equation:

$$\frac{c}{q} = \frac{c}{q_\infty} + \frac{1}{q_\infty a}$$

where q, c and a are the amount of mercury(II) adsorbed (mg/g), the equilibrium concentration (mg/l.) and the equilibrium constant (l./mg), respectively. The q_∞ values for MR-50 and XAD-4 were calculated to be 42.1 and 55.6 mg/g, respectively.

Table 3 summarizes the adsorption behaviour of mercury(II) on MR-50 and XAD-4 from strong acid media. The amount of adsorption of mercury(II) decreases with increase of acid concentration. The adsorption of mercury(II) is greatly reduced in hydrochloric acid. This observation may be explained by assuming the formation of complex mercury(II)

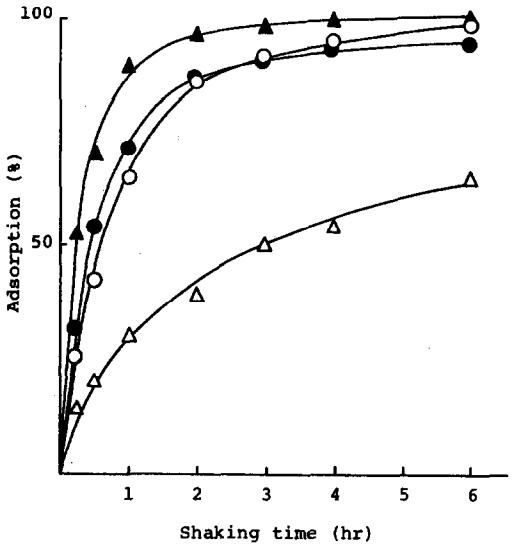

Fig. 1. Effect of shaking time on adsorption of mercury(II) on MR-50 and XAD-4, —●— MR-50 (pH 5.0), —▲— XAD-4 (pH 5.0), —○— MR-50 (0.01*M* HNO_3), —△— XAD-4 (0.01*M* HNO_3).

anions such as $HgCl_4^{2-}$ and $HgCl_3^-$, which have a low affinity for polymer beads.

A similar effect was observed in the presence of neutral salts at pH 5.0. As shown in Table 4, mercury(II) adsorption is affected by the presence of sodium chloride and potassium chloride, present at high concentration in a 0.001*M* mercury(II) solution. Sanemasa *et al.*[7] have reported that loss of mercury(II), kept in a polyethylene container, can be prevented by the addition of sodium chloride, in agreement with the present work, *i.e.*, the marked reduction in the amount of mercury(II) adsorbed in the presence of chloride ion. A reduction in the amount of mercury(II) adsorbed was also clearly observed in the presence of EDTA.

So far, the mechanism of the adsorption of mercury(II) has not been identified. It may be associated with various chemical forms of mercury(II), such as Hg^{2+}, $Hg(OH)^+$, $HgCl_2$ and $Hg(OH)_2$, because the adsorption takes place over a wide range of pH values.

The adsorption of mercury(II) on columns of polymer beads in the presence of foreign metal ions was also studied. When a column packed with 4 g of MR-50 was used, the presence of silver, cadmium, cobalt(II), copper(II), nickel and zinc did not interfere

Table 2. Adsorption of mercury(II) from acidic media on polymer beads*

Media	Adsorption, % G-50	MR-7.5	MR-15	MR-30	MR-50	XAD-2	XAD-4
0.1*M* HNO_3	1.0	2.2	4.9	20.3	88.6	78.6	89.4
0.01*M* HNO_3	1.1	1.2	4.4	19.4	97.3	83.9	95.0
Acetate buffer, pH 5.0	1.1	1.8	4.5	23.7	97.0	85.0	97.5

* Mercury solution: $1 \times 10^{-3}M$ $Hg(NO_3)_2$, 10 ml. Polymer beads: 100 mg. Shaking time: 24 hr.

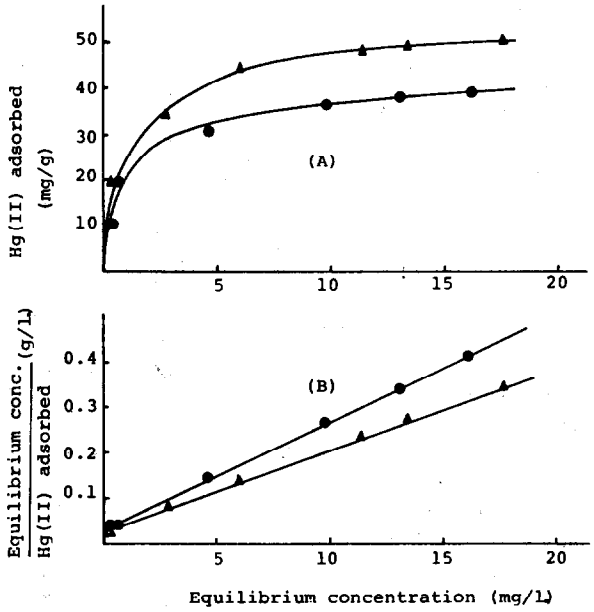

Fig. 2. Adsorption isotherms of mercury(II) on MR-50 (—●—) and XAD-4 (—▲—) (A) Langmuir plot (B) at 20°.

Table 3. Adsorption of mercury(II) on MR-50 and XAD-4 from acidic media*

Acid	Concentration, *M*	Adsorption, % MR-50	Adsorption, % XAD-4
HNO_3	1	64.0	70.4
	0.1	88.6	89.4
	0.01	97.3	95.0
HCl	1	6.7	10.0
	0.1	6.6	14.5
	0.01	6.8	14.5
	0.001	96.8	97.0
$HClO_4$	1	58.0	78.7
	0.1	88.0	89.4
	0.01	96.3	94.2
H_2SO_4	0.1	82.7	84.7
	0.01	96.7	95.7
H_2O	—	97.0	97.5

* Conditions as in Table 2.

Table 4. Adsorption of mercury(II) from various salt solutions (pH 5.0) on MR-50*

Salt	Concentration, *M*	Adsorption, %
NaCl	0.01	66.9
	0.001	94.8
	0.0001	96.9
KCl	0.01	69.9
	0.001	95.0
	0.0001	97.2
$NaNO_3$	0.01	96.9
	0.001	97.0
KNO_3	0.01	96.6
	0.001	97.2

* Conditions as in Table 2.

with the adsorption of mercury(II) from 100 ml of $5 \times 10^{-5} M$ mercuric nitrate (pH 5.0, acetate buffer) containing 100 times as much foreign ion as mercury(II).

Table 5 shows the recovery of mercury(II) from MR-50 and XAD-4 columns with hydrochloric acid and sodium chloride solutions. Although the interference caused by the chloride would be expected to promote the elution of the mercury(II), the effect of sodium chloride solution as an effluent was negligible. In the case of MR-50, mercury(II) could be recovered with 8 bed-volumes of hydrochloric acid ($>0.1 M$) and a sharp elution curve was obtained, as shown in Fig. 3, but 17 bed-volumes of $1 M$ hydrochloric acid were required for the recovery of mercury(II) from the XAD-4 column (Fig. 3).

In conclusion, XAD-4 is superior to MR-50 in the adsorption of mercury(II), but MR-50 give the better recovery. The surface area of the polymer beads influences the adsorption of mercury(II), while the desorption of mercury(II) may be affected by other properties of the polymer beads, such as pore size and pore volume. It is known that activated carbon adsorbs heavy metal ions, especially mercury(II), in the presence of hydrochloric acid.[8,9] However, its adsorption behaviour is different from that of the polymer beads, which have a low affinity for the complex anions of mercury(II). Application of polymer beads in the separation and selective enrichment of mercury(II) may be of interest in water purification. However, the range of application is limited because the affinity for mercury(II) decreases in the presence of chloride ions and chelating agents. The polymer beads may be useful in the selective removal of mercury(II) from strongly acidic solutions, with the

Table 5. Recovery of mercury by column operation

Eluent		Eluent volume, *ml*	Recovery of mercury, % MR-50	XAD-4
HCl	0.01*M*	100	73.8	0
		200	82.1	0
	0.1*M*	100	95.1	1.6
		200	—	14.8
	1*M*	100	96.6	85.1
		200	—	95.7
NaCl	1*M*	200	3.1	0

exception of hydrochloric acid. The high stability of the polymer beads, which have no reactive functional groups, suggests that they are suitable for repetitive long-term use. The MR type polymer beads, including XAD-2 and -4, are often used as a support in extraction chromatography,[10,11] and so particular attention should be paid to the adsorption of mercury(II) on the polymer matrix.

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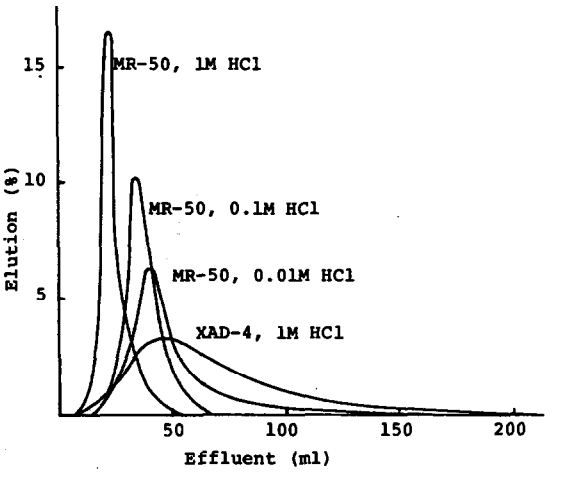

Fig. 3. Typical elution curves of mercury(II).

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EXTRACTION OF ALKALI METAL PICRATES WITH POLY- AND BIS(CROWN ETHER)S

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Summary—Extraction of alkali metal picrates by new poly- and bis(crown ether)s containing benzo-15-crown-5 and benzo-18-crown-6 moieties was carried out with chloroform as water-immiscible solvent. The poly- and bis(crown ether)s were found to extract the picrates more effectively than the corresponding monocyclic crown ethers. In particular, poly- and bis(benzo-15-crown-5), and bis(benzo-18-crown-6) are remarkably effective extracting reagents for potassium and rubidium, and for caesium, respectively. Extraction equilibrium constants and the complexation constants in the chloroform phase were also evaluated and the contribution of the complexation constants to the extractability is discussed.

Solvent extraction is one of the most important techniques of analytical chemistry, and has been applied to separation of ions and to pretreatment in various analyses. Macrocyclic polyethers, compounds commonly referred to as crown ethers, are known to have attractive cation-complexing abilities, which result in conversion of inorganic cations into lipophilic species. This property of crown ether derivatives has been utilized in solvent extraction.[1–4] Moreover, since the complexing properties of the crown ether derivatives depend on the relative sizes of the cation and the hole in the crown ether ring, the number and variety of hetero atoms, and other structural factors, their selectivity in complexing cations varies and causes some selectivity in the extraction of cations. Conversely, solvent extraction can be applied for rapid screening of the cation-complexing ability of crown ethers.

It seems likely that poly- and bis(crown ether)s containing more than one adjacent crown ether moiety may exhibit a kind of co-operative effect in complexing cations, especially by forming sandwich-type 2:1 complexes,[5–7] and such complexes are generally more lipophilic than those of the corresponding monocyclic crown ethers. These compounds are, therefore, expected to be effective extracting reagents for various cations.

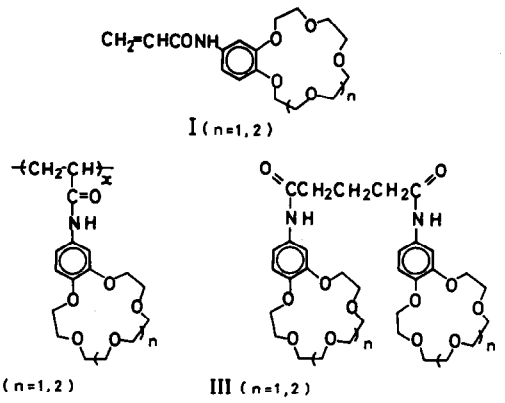

Fig. 1. Crown ether derivatives used in this study.

The poly- and bis(crown ether)s **II** and **III** (n = 1,2) shown in Fig. 1 have already been reported as new extracting reagents.[8] This paper deals in detail with their use for the extraction of alkali metal cations. In this study, chloroform was chosen as the water-immiscible solvent and the picrates as the alkali metal salts. Attempts were also made to determine extraction equilibrium constants and complexation constants in the chloroform phase.

EXPERIMENTAL

Materials

The synthesis of the monocyclic crown ether **I** (n = 1,2) and the poly- and bis(crown ether)s **II** and **III** (n = 1,2) has been described elsewhere.[8] Sodium, potassium, rubidium and caesium picrates were prepared according to Fuoss's method.[9] The chloroform was purified by washing it several times with water, followed by fractional distillation. Demineralized water was used. The solvents were saturated with each other before use, to prevent volume changes in the phases during extraction. The concentration of the poly- and bis(crown ether) chloroform solutions is defined in terms of the number of crown ether monomer units, *e.g.*, for **II**, $C_{II} = x \times$ nominal polymer concentration.

Extraction

Equal volumes (10 ml) of chloroform solution of crown ether and aqueous alkali metal picrate solution were introduced into a stoppered flask, and shaken for 40 min at 25 ± 0.1°. After phase separation, 3 ml of acetonitrile were added to 3 ml of the chloroform phase, and the picrate concentration in the mixture was determined by measuring the absorbance. The molar absorptivities of the extracted complexes were estimated in a separate experiment (λ_{max} 374 nm; ϵ Na^+ 1.86×10^4, K^+ 1.87×10^4, Rb^+ 1.88×10^4, Cs^+ 1.86×10^4 $l.mole^{-1}.cm^{-1}$). Distribution constants (K_d) of the alkali metal picrates in the absence of crown ether were determined as follows. Equal volumes (200 ml) of picrate solutions of known concentrations in demineralized water and of chloroform were shaken at 25°. The phases were left for 20 hr to separate and clarify. Half

Table 1. Distribution ratio in extraction of alkali metal picrates with crown ethers I, II and III (25°C)

Crown ether	log D			
	Na^+	K^+	Rb^+	Cs^+
I (n = 1)	(−2.28)[a]	−1.94	−2.28	(−3.15)[a]
II (n = 1)	−1.66	(0.097)[b]	(−0.284)[b]	−1.05
III (n = 1)	−2.21	−0.565	−0.747	−1.51
I (n = 2)	(−2.21)[a]	−1.16	−1.64	−2.05
II (n = 2)	−1.54	−0.669	−0.832	−0.926
III (n = 2)	−2.82	−0.952	−0.986	−0.620

Crown ether concentration for crown unit: $5 \times 10^{-4}M$.
Picrate concentration: except a and b, $1 \times 10^{-3}M$; a, $1 \times 10^{-2}M$; b, $1 \times 10^{-4}M$.
[a] D is too small to determine spectrophotometrically for $1 \times 10^{-3}M$ picrate.
[b] Some precipitate was observed for $1 \times 10^{-3}M$ picrate.

the chloroform phase (100 ml) was evaporated to dryness and the residue taken up in 5 ml of acetonitrile. The concentration of picrate in this solution was then determined spectrophotometrically and the values of K_d were calculated by use of equation (8) (K_d: Na^+ 1.20×10^{-3}, K^+ 2.67×10^{-3}, Rb^+ 3.66×10^{-3}, Cs^+ 6.60×10^{-3} l./mole).

RESULTS AND DISCUSSION

Distribution ratio

Extractions were carried out at 25° from 1×10^{-2}–$1 \times 10^{-4}M$ aqueous alkali metal picrate solution with 1×10^{-4}–$5 \times 10^{-4}M$* poly- and bis-(crown ether) solutions in chloroform. For comparison, their monomeric analogues I (n = 1,2) were also used. The results are expressed as D, the distribution ratio of alkali metal cation between the two phases. The results of extraction with $5 \times 10^{-4}M$ crown ether solution are shown in Table 1. Assuming that the metal cations are transferred to the chloroform phase as 1:1 complexes of cation and crown ether, the theoretical maximal value of D is 1 (log D = 0) for the initial picrate concentration of $1 \times 10^{-3}M$. On the other hand, for 2:1 crown ether-cation stoichiometry of complex formation, the maximal value is 0.333 (log D = −0.48) for the same initial picrate concentration. According to the D values obtained for the same conditions, poly- and bis(crown ether)s II and III (n = 1,2) give higher log D values than their monomeric analogues I (n = 1,2). It is particularly noteworthy that the values for the potassium–bis-(crown ether) III (n = 1) and caesium–bis(crown ether) III (n = 2) system approach the theoretical maximum for 2:1 stoichiometry.

It is known that these two cations can form sandwich-type 2:1 crown ether-cation complexes with benzo-15-crown-5 or benzo-18-crown-6,[10] and the bis(crown ether)s could easily form 2:1 complexes with these cations by co-operative action of the two adjacent crown ether units. This co-operative effect may explain the increase in distribution coefficient with these polymeric crown ethers.

* *i.e.*, moles of monomer unit (benzo-15-crown-5 or benzo-18-crown-6) per litre.

Extraction equilibrium constant K_e

The extraction equilibrium between an aqueous solution of metal cation (M^+), picrate anion (A^-) and a chloroform solution of crown ether (CE) can be defined for the 1:1 crown ether-cation complex by the equations

$$M^+_{aq} + A^-_{aq} + CE_{org} \rightleftharpoons M(CE)A_{org}$$

$$K_e = [M(CE)A]_{org}/([M^+]_{aq}[A^-]_{aq}[CE]_{org}). \quad (1)$$

Attempts were made to estimate the K_e value graphically.[4] Since chloroform is used as the organic solvent, the dissociation of the ion-pair M(CE)A is negligible,[6] and the concentration of uncomplexed cation in the chloroform phase is extremely low compared with that of the complex. The concentration of crown ether in the aqueous phase was also confirmed to be quite low, in a preliminary experiment. The following assumptions can, therefore, be made:

$$[M(CE)A]_{org}/[M^+]_{aq} = D \quad (2)$$

$$[M^+]_{aq} = [A^-]_{aq} = M^\circ - A \quad (3)$$

$$[CE]_{org} = (CE)^\circ - A \quad (4)$$

where M° and $(CE)^\circ$ denote the initial concentrations of alkali metal and crown ether, respectively, and A the concentration of picrate transferred to the organic phase, which can be determined spectrophotometrically. Equation (1) can then be rewritten as equation (5).

$$D = K_e(M^\circ - A)[(CE)^\circ - A] \quad (5)$$

If these assumptions are reasonable, the plots of $-\log D$ *vs.* $-\log (M^\circ - A)[(CE)^\circ - A]$ should give a straight line with a slope of 1, and log K_e could be obtained from the intercept of the straight line.

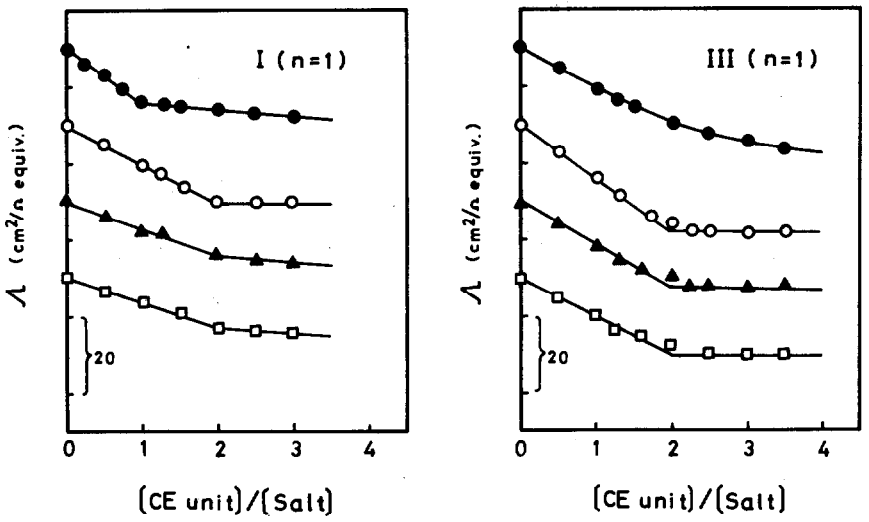

Fig. 2. Plots of equivalent conductance Λ *vs.* the ratio [CE unit]/[salt], for **I** and **III** ($n = 1$) systems [Salt]: 5×10^{-4} *M* BPh_4 in acetone, at 25°C. Na^+ (●), K (○), Rb^+ (▲), Cs^+ (□).

If 2:1 complexes of crown ether and metal cation exist (which occurs mainly in the monocyclic crown ether systems) equation (6) can be applied.

$$D = K_e(M^\circ - A)[(CE)^\circ - 2A]^2 \quad (6)$$

However, 2:1 complexes of this type, formed by a cation and two separate crown ether units, are produced by poly- and bis(crown ether)s only when the concentration of the crown ether is extremely high. That is to say, the poly- and bis(crown ether)s mainly form the 2:1 complexes only intramolecularly. Consequently, two adjacent crown ether units of the poly- and bis(crown ether)s can be considered as a single entity, and equation (7) can be used.

$$D = K_e(M^\circ - A)[(CE)^\circ - 2A] \quad (7)$$

The stoichiometry of the complexes was determined indirectly by measuring the conductance of alkali metal tetraphenylborate–crown ether acetone solutions at 25°. Plots of equivalent conductance Λ *vs.* the ratio [CE unit]/[Salt] for the monocyclic crown ether **I** ($n = 1,2$) and bis(crown ether) **III** ($n = 1,2$) systems are shown in Figs. 2 and 3. It is considered from the break-points of the plots that monocyclic crown ether **I** ($n = 1$) forms a 1:1 complex with sodium and 2:1 complexes with the other three cations. Monocyclic crown ether **I** ($n = 2$) forms 1:1 complexes with all four cations. In addition, bis(crown ether) **III** ($n = 1$) gives 2:1 complexes with potassium, rubidium and caesium, and bis(crown ether) **III** ($n = 2$) does so with caesium. The plots for the other bis(crown ether) **III** ($n = 1,2$) systems show

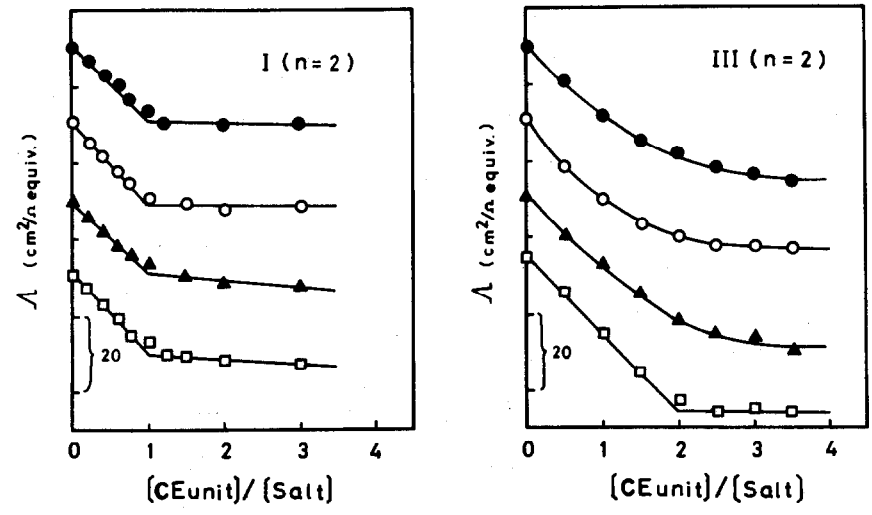

Fig. 3. Plots of equivalent conductance Λ *vs.* the ratio [CE unit]/[salt] for **I** and **III** ($n = 2$) systems [Salt]: 5×10^{-4}*M* BPh_4 in acetone, at 25°C. The symbols are identical with those in Fig. 2.

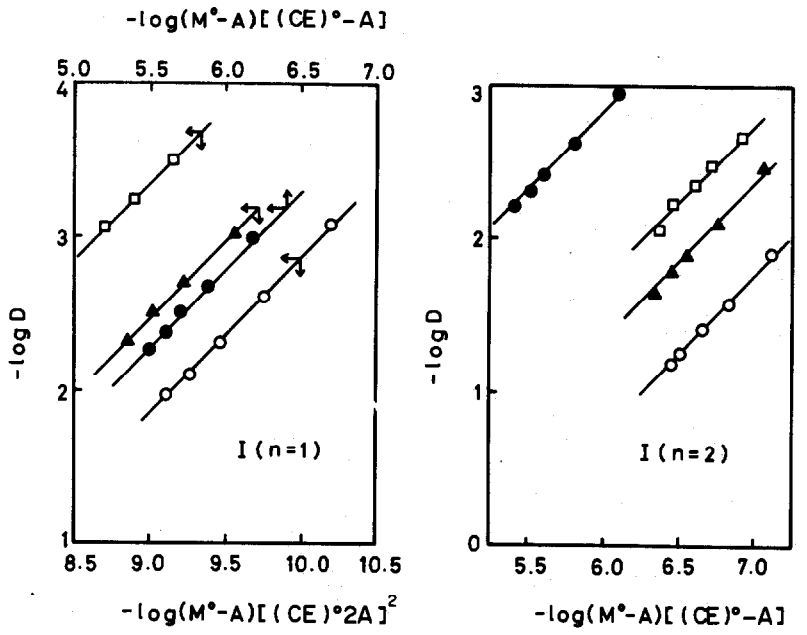

Fig. 4. Plots of $-\log D$ *vs.* $-\log (M^\circ - A)[(CE)^\circ - xA]^x$ for **I** (n = 1,2) systems (x = 1 or 2). Na^+ (●), K^+ (○), Rb^+ (▲), Cs^+ (□).

smooth curves although some of them could be interpreted as indicating 2:1 complex formation. Efforts were made to use the same technique to elucidate the stoichiometry of complexes formed by the poly(crown ether) but no sharp break-point was observed because of increasing steric hindrance or electrostatic repulsion as the fraction of the crown ether complexes increased.[11] However, the poly(crown ether)s are expected to resemble the corresponding bis(crown ether)s in the stoichiometry of complex formation.

On the basis of this assumption, plots were made for equations (5), (6) and (7),.

All gave straight lines with slopes of approximately 1, which indicates that the assumption is reasonable. Figure 4 shows a typical set of plots. In the potassium, rubidium and caesium systems with crown ether **I** (n = 1), some deviation from the straight line was observed at lower crown ether concentrations or higher picrate concentrations than used here, which suggests a change of stoichiometry from 2:1 to 1:1. From the intercepts of these plots the values of log K_c were calculated, and these are tabulated in Table 2.

Although the K_c values derived from different equations cannot be compared directly, the values derived from the same equation can. If the extractability is dependent only on the distribution constant of the alkali metal picrates in the absence of a crown ether, the order should be $Cs^+ > Rb^+ > K^+ > Na^+$. However, the order found is quite different. In particular, the high K_c values for the potassium and rubidium systems of poly- and bis(crown ether)s **II, III** (n = 1) and the caesium system of bis(crown ether) **III** (n = 2) are remarkable. The complexing properties of the crown ethers must also play an important role in determining the extractability.

Complexation constant for the chloroform phase

The extraction equilibrium for the 1:1 complexes may be broken down into the following set of equilibria,[6,12]

$$M^+_{aq} + A^-_{aq} \rightleftharpoons MA_{org}$$

$$K_d = [MA]_{org}/[M]_{aq}[A^-]_{aq} \quad (8)$$

$$MA_{org} + (CE)_{org} \rightleftharpoons M(CE)A_{org}$$

$$K_c = [M(CE)A]_{org}/[MA]_{org}[(CE)]_{org} \quad (9)$$

$$K_c = K_d K_c \quad (10)$$

where K_d and K_c refer to the distribution constant of the alkali metal picrate for the absence of a crown ether and the complexation constant in the chloroform phase, respectively. K_c can be estimated from

Table 2. Extraction equilibrium constants (K_c) at 25°C

Crown ether	log K_c			
	Na^+	K^+	Rb^+	Cs^+
I (n = 1)	3.10	(7.10)	(6.54)	(5.59)
II (n = 1)	3.80	7.75	7.20	5.44
III (n = 1)	3.46	6.63	6.13	4.85
I (n = 2)	3.16	5.22	4.64	4.24
II (n = 2)	3.61	5.82	5.59	5.62
III (n = 2)	3.41	5.46	5.35	6.36

The units for K_c are $l^2/mole^2$ ($l^3/mole^3$ for values in parentheses).

Table 3. Complexation constants for the chloroform phase at 25°C

Crown ether	log K_e			
	Na^+	K^+	Rb^+	Cs^+
I ($n = 1$)	6.02	(9.67)	(8.98)	(7.77)
II ($n = 1$)	6.72	10.3	9.64	7.62
III ($n = 1$)	6.38	9.20	8.57	7.03
I ($n = 2$)	6.08	7.79	7.08	6.42
II ($n = 2$)	6.53	8.39	8.03	7.80
III ($n = 2$)	6.33	8.03	7.79	8.54

The units for K_e are l/mole (l^2/mole^2 for values in parentheses).

equation (10), provided K_d is known. In the preliminary experiments, the K_d values of these four alkali metal picrates were determined at 25° (see Experimental). In extraction of the 2:1 complexes, the K_c values can be obtained in a similar manner. The K_c values are summarized in Table 3.

Comparisons can be made between K_c values for complexes with identical stoichiometry and dimensions. For 1:1 complexes, bis(crown ether)s **III** ($n = 1,2$) give slightly higher K_c values for a given cation than their monomeric analogue **I** ($n = 1,2$), and the poly(crown ether)s **II** ($n = 1, 2$) give still higher values than the bis(crown ether)s. This suggests that some co-operative effect of adjacent crown ether units may influence the complexation of metal cations with the poly- and bis(crown ether)s. However, for the 2:1 complexes, the poly(crown ether) systems do not have the same K_c values for a given cation as the bis(crown ether) systems, and this cannot be explained simply in terms of co-operative effects of neighbouring crown ether moieties in forming the 2:1 complex. It is, however, safe to say that the high extractability and selectivity of these complexes of poly- and bis(crown ether)s with alkali metal cations are mainly a consequence of the high K_c values.

The K_c values for the 2:1 complexes of poly- and bis(crown ether)s seem to depend partly on the chain-length between two adjacent crown ether moieties.[7] It is also of interest to see how the chain length of bis(crown ether)s affects their extractability.

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NON-DISPERSIVE ATOMIC-FLUORESCENCE SPECTROMETRY OF TRACE AMOUNTS OF BISMUTH BY INTRODUCTION OF ITS GASEOUS HYDRIDE INTO A PREMIXED ARGON (ENTRAINED AIR)–HYDROGEN FLAME

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Summary—A method has been developed for the determination of bismuth by generation of its gaseous hydride and introduction of the hydride into a premixed argon (entrained air)–hydrogen flame, the atomic-fluorescence lines from which are all detected by use of a non-dispersive system. The detection limit is 5 pg/ml, or 0.1 ng of bismuth, but the reagent blank found in a 20-ml sample volume was approximately 2 ng of bismuth. Analytical working curves obtained by measuring peak-heights and integrated peak-areas of the signals are linear over a range of about four orders of magnitude from the detection limit. Perchloric, phosphoric and sulphuric acids up to 2.0*M* concentration give no interference, but nitric acid gives slight depression of the signal. The presence of silver, gold, nickel, palladium, platinum, selenium and tellurium in 1000-fold ratio to bismuth causes pronounced depression of the signal, whereas mercury and tin slightly enhance the atomic-fluorescence signal. The method has been applied to the determination of bismuth in aluminium-base alloys and sulphide ores with use of the standard additions method. The results are in good agreement with those obtained by flame atomic-absorption spectrometry and optical emission spectrometry with an inductively coupled plasma.

In atomic-fluorescence spectrometry by direct nebulization of solutions into a flame, some authors[1–13] have reported detection limits in the 0.005 10 μg/ml range for bismuth, with a dispersive system mostly used at 302.5 and 306.8 nm and a high-intensity hollow-cathode lamp or microwave-excited electrodeless discharge lamp (EDL) as narrow-line excitation source, and others[7,13,14] have obtained detection limits of 0.2–200 μg/ml by using a xenon arc lamp as a continuum excitation source. Larkins[11] has reported a detection limit of 0.25–30 μg/ml of bismuth with a non-dispersive system. The atomic-fluorescence method has successfully been applied to the determination of bismuth in steels.[15,16] Weeks *et al.*[17] have obtained a detection limit of 3 ng/ml by using a pulsed tunable dye-laser as an excitation source. All these authors have used air–hydrogen, air–acetylene (normal or separated), oxygen–hydrogen or argon (entrained air)–hydrogen flames for the atomization. Clyburn *et al.*[18] have obtained a bismuth detection limit of 10 ng/ml at 306.8 nm by employing a specially designed graphite furnace and a 150-W xenon arc continuum.

On the other hand, in atomic-absorption spectrometry, the sensitivity for bismuth has been markedly improved by using a hydride-generation technique based on reduction of bismuth to its hydride BiH_3 (bismuthine) with sodium borohydride (or $TiCl_3$ and Mg rod),[19] introduction of the generated gaseous bismuthine into an atom reservoir, such as an argon entrained air)–hydrogen flame,[19–25] heated silica tube[26–28] or heated graphite furnace.[22] The detection limits obtained range from 1 to 50 ng of bismuth. Moreover, Thompson *et al.*[29,30] have applied the hydride-generation technique to the determination of bismuth by optical emission spectrometry with an inductively coupled plasma and obtained a detection limit of 0.8 ng/ml for bismuth, which is better by a factor of about 50 than that obtained by utilizing a conventional direct nebulization of solutions. However, there has so far been no paper on the combination of atomic-fluorescence spectrometry for bismuth with a hydride-generation technique.

Recently we constructed a versatile atomic-fluorescence spectrometer which can be easily used for dispersive and non-dispersive systems and have demonstrated its performance for determination of mercury,[31] arsenic[32,33] and antimony[34] (on essentially the principle described by Thompson[35]). Dagnall *et al.*[1] and Hobbs *et al.*[10] have made thorough studies of the spectral characteristics of all the atomic-fluorescence lines of bismuth. In our preliminary study, the non-dispersive atomic-fluorescence sensitivity for bismuth was found to be at least two orders of magnitude better than that obtained with the dispersive system at the 206.2, 302.5 and 306.8-nm atomic-fluorescence lines of bismuth. The non-dispersive system has the advantage of higher throughput (larger solid angle, exit and input apertures and higher transmission) and simultaneous measurement of all the fluorescence lines, but is susceptible to increased flame background noise and sometimes to spectral interfer-

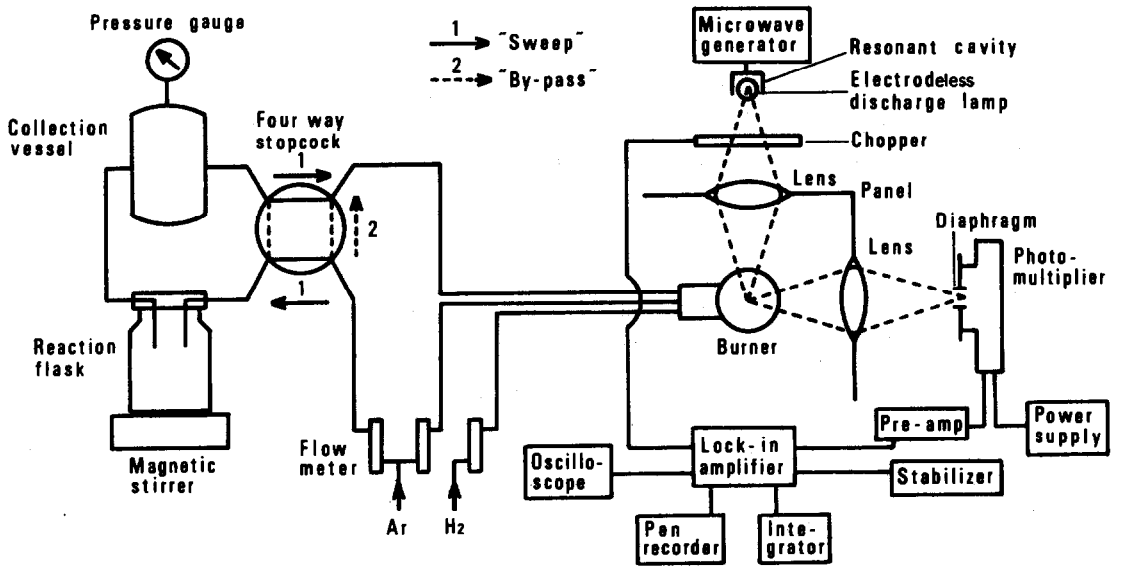

Fig. 1. Schematic diagram of the experimental system.

ence. This paper describes the non-dispersive atomic-fluorescence spectrometry of bismuth by use of a hydride-generation technique and a premixed argon (entrained air)–hydrogen flame with a home-made burner, and its application to the determination of bismuth in aluminium-base alloys and sulphide ores.

EXPERIMENTAL

Reagents

All reagents used were of analytical-reagent grade, unless otherwise stated. The stock standard solution of bismuth (1000 μg/ml) was prepared by dissolving 1.00 g of high-purity bismuth metal (99.999%) in 10 ml of concentrated nitric acid and diluting to 1 litre with distilled water. Dilute bismuth solutions were prepared immediately before use by dilution of the stock solution

Portions of sodium borohydride (30–100 mg) were weighed, wrapped in a sheet of wafer (9 cm diameter, Kodomo–Odori Oblate Co.) and stored in a desiccator. In our preliminary study, bismuthine was found to be much more efficiently produced by sodium borohydride as reductant than by zinc and tin(II) chloride, so this reagent was used throughout this work. The wafer was made of starch and agar-agar.

Instrumentation

A block diagram of the experimental arrangement is given in Fig. 1. The components are listed in Table 1.

Table 1. Experimental components

Item	Description and manufacturer
Light-source and power	
Lamp	Bismuth EDL, laboratory-made
Power supply	Microtron 200, 2450 ± 25 MHz, Electro-Medical Supplies
Resonant cavity	Model 214 L, 1/4-wave resonant cavity, Electro-Medical Supplies
Light chopper	Laboratory-made
Lenses	30 mm diameter, 75 mm focal length, quartz
Burner	Laboratory-made
Nebulizer chamber	Techtron
Gas controller	Laboratory-made
Photomultiplier	R-166 UH, "solar-blind" type, Hamamatsu TV
Housing	Nippon Jarrell-Ash
Diaphragm	C-25, Chuo Precision Industrial
Power supply	412 B, John-Fluke
Pre-amplifier	Jp 406, Nippon Jarrell-Ash
Power supply	±15 V, Laboratory-made
Lock-in amplifier	572 B, NF Circuit Design Block
Line-power stabilizer	A-133, NF Circuit Design Block
Oscilloscope	CS-1351, Trio
Pen recorder	QPD_{54}, Hitachi
Digital integrator	RD-01, Tokyo Kagaku
Hydride generation unit	ASD-1A, Nippon Jarrell-Ash

The right half of Fig. 1 represents a non-dispersive atomic-fluorescence spectrometer with flame atomization. For a dispersive measuring system, the photomultiplier (with housing) is readily replaced by a monochromator (0.3-m Ebert mounting, Model JE-30, Nippon Jarrell-Ash Co.) equipped with another photomultiplier (R-106 UH, Hamamatsu TV Co.). Light from a bismuth EDL is focused by a single lens into the centre of a premixed argon (entrained air)–hydrogen flame at a fixed height above the burner top. The diameter of the focused beam at the centre of the flame is approximately 5 mm. The atomic-fluorescence radiation is measured at right angles to the axis of the optical path from the light source to the flame. A nitrogen-sheathed, water-cooled burner (18 mm in diameter), already described in detail,[32] is fitted on a Techtron nebulizer chamber. The position of the burner/nebulizer system is laterally and vertically adjusted with a screwed cramp (Nippon Jarrell-Ash Model HR-65).

We have successfully prepared a number of EDL sources for bismuth by the general method described elsewhere.[31] The bismuth lamps, fabricated from "Suprasil" quartz tubing, were 33 mm in length, with 10 mm outer diameter and 1 mm wall thickness, and contained *ca.* 6 mg of bismuth tri-iodide. They were sealed at a final argon pressure of 2 mmHg (*ca.* 266 Pa). The EDL sources prepared in this work were operated in a resonant cavity with air-cooling to the base of the lamp.

Procedure and experimental conditions

The experimental conditions used throughout this study are summarized in Table 2. All components were operated according to the manufacturers' directions except where otherwise noted.

The sample solution is transferred to a reaction flask, a known amount of hydrochloric acid is added and the mixture is diluted to approximately 20 ml with distilled water. A packet of sodium borohydride powder is added and the reaction flask is immediately connected to the apparatus with the argon flow by-passing it, with the four-way stopcock in the "by-pass" position. The mixture is agitated with a magnetic stirrer and the reaction is allowed to continue at room temperature. The four-way stopcock is then turned to the "sweep" position, allowing the argon to carry the bismuthine into the flame. The atomic-fluorescence signal is simultaneously recorded both on a pen-recorder for peak-height measurement and on a digital integrator for peak-area measurement. After recording of the signal, the four-way stopcock is again turned to the "by-pass" position and the reaction flask is removed from the apparatus. Argon serves both as carrier gas and as auxiliary gas for the premixed argon (entrained air)–hydrogen flame.

The amount of bismuth in the test solutions used throughout this work was 400 ng, equivalent to 20 ng/ml, except where stated otherwise. Blanks were run throughout, and their values subtracted from the gross values to obtain the net values reported here.

RESULTS AND DISCUSSION

Comparison of EDLs and dispersive study

Thorough studies of the atomic fluorescence of bismuth[1,9,10] have made it clear that bismuth fluorescence can be easily excited either with an iodine EDL (owing to spectral overlap of the bismuth resonance line at 206.17 nm with the iodine line at 206.16 nm) or with a bismuth EDL. It was ascertained in our previous work[34] that the antimony EDL available emitted the very intense 206.16-nm iodine line, possibly because of the antimony tri-iodide contained in the lamp. In our preliminary work the most useful bismuth EDL prepared in this laboratory was compared with the above-mentioned antimony EDL (EMI Electronics, operated in an EMS 211 L 3/4-wave resonant cavity, Electro-Medical Supplies Ltd., without air-cooling) and an iodine EDL (Hamamatsu TV, Type L978, operated with a Hamamatsu TV microwave power supply, Model C977). Table 3 shows the relative emission intensities of the bismuth lines observed from the three EDLs and the relative atomic-fluorescence intensities observed at four major bismuth lines under optimum source and flame conditions. With the non-dispersive system the relative atomic-fluorescence intensities were found to be 100, 15.6 and 8.0 at the 200-ng bismuth level with the Bi-, Sb- and I_2-EDLs, respectively. As a result, the bismuth EDL was used as the source for excitation of line spectra throughout the following study.

Table 2. Experimental conditions for the non-dispersive measurement of bismuth atomic-fluorescence

Microwave power for EDL	32 W (incident power, 35 W; reflected power, 3 W)
Flow-rate of air for cooling EDL	6.0 l./min
Photomultiplier voltage	400 V
Diaphragm aperture	5.0 mm
Load resistance	470 kΩ
Modulation frequency	240 Hz
RC time constant	1.0 sec
Integration time for peak-area measurement	15 sec
Sample size	20 ml
Amount of sodium borohydride	0.05 g
Acidity	1.0*M* HCl
Reaction time	60 sec
Flame	
Hydrogen flow-rate	1.0 l./min
Argon flow-rates	4.0 l./min for carrier gas and 1.5 l./min for auxiliary gas
Flame height	50 mm above the top of burner head

Table 3. Source emission and atomic-fluorescence intensities of bismuth lines with electrodeless discharge lamps

Wavelength, nm	Relative emission intensity of source*			Relative atomic-fluorescence intensity†		
	Bi-EDL§	Sb-EDL§	I_2-EDL§	Bi-EDL§	Sb-EDL§	I_2-EDL§
206.17	25	10	3	4.3	7.5	1.9
269.67	7	—¶	—¶	0.9	—¶	—¶
302.46	89	—¶	—¶	4.1	5.7	1.4
306.77	100	—¶	—¶	100	2.1	1.1

* Relative to 100 for the bismuth emission line at 306.77 nm. All values obtained with identical measuring conditions.

† Relative to 100 for the atomic-fluorescence line at 306.77 nm. All values obtained for 2000 ng Bi with identical measuring conditions.

§ Operated at 32, 19 and 10 W for Bi-, Sb- and I_2-EDLs, respectively, which gave the most intense and stable emission.

¶ Not measurable.

Effect of flame composition and flame height

To find the optimum flame conditions the hydrogen flow was varied in the range 1.0–5.0 l./min with the total flow of argon kept constant at 6.0 l./min. The results obtained with peak-height measurement are shown in Fig. 2, together with the flame noise. The flame height is the distance from the top of the burner head to the level of the centre of the diaphragm attached to the photomultiplier housing. The fluorescence intensity and flame noise were more affected by hydrogen flow-rate than by flame height. The optimum conditions are shown in Table 2. At a hydrogen flow-rate below 1.0 l./min the flame was often extinguished. The flow-rate of nitrogen as a sheath gas for the flame was fixed at 1.0 l./min throughout this work.

Effect of flow-rate of carrier gas

The fluorescence intensity increased with carrier-gas flow-rate in the range 2.0–5.0 l./min at different auxiliary gas flow-rates in the range 1.0–3.0 l./min. However, the reproducibility became exceedingly poor if the flow-rate of carrier gas was greater than about 5.0 l./min. Below 3.0 l./min flow of a carrier gas, though there was little or no variation in the atomic-fluorescence intensity by peak-area measurement, the fluorescence signal was broadened because of slow introduction of the generated bismuthine into the flame, resulting in a decreased peak-height. The optimum flow-rates of argon as carrier and auxiliary gas are shown in Table 2.

Effect of amount of sodium borohydride and reaction time

For bismuthine generation the sodium borohydride is generally added as an alkaline solution[23,26–28] or as a pellet.[19–21,24,25] In this work, however, it was wrapped in a wafer sheet, on account of the characteristics of the generation unit. The effect of the amount of sodium borohydride was examined in the range 0.03–0.1 g. More than 0.1 g caused poorer reproducibility of the signals, because of rapid introduction of the excess of hydrogen at high pressure into the flame. The fluorescence intensity was maximal when around 0.05 g of borohydride was used. The reaction time of 60 sec was sufficient to complete the generation of bismuthine.

Effect of acidity

All samples and blanks were acidified with hydrochloric acid, as generally described in atomic-absorption spectrometry.[19–23,25–28] Varying the acidity from 0.1 to 2.0*M* scarcely affected the bismuth signal but the signal from the reagent blank increased to some extent with an increase in acid concentration. The optimum acidity was 1.0*M*.

Analytical working curve, sensitivity and precision

Under the optimum conditions (Table 2), analytical working curves were obtained by using freshly pre-

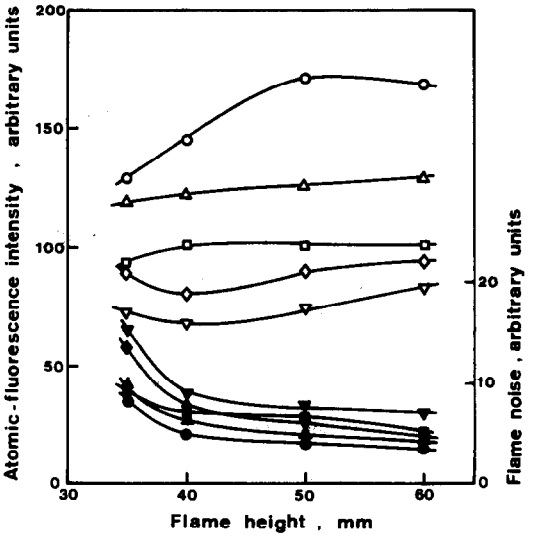

Fig. 2. Effect of flame conditions on bismuth atomic-fluorescence intensity (H_2 flow-rates, l./min: ○, 1.0; △, 2.0; □, 3.0; ◇, 4.0; ▽, 5.0) and flame noise (H_2 flow-rates, l./min: ●, 1.0; ▲, 2.0; ■, 3.0; ◆ 4.0; ▼, 5.0).

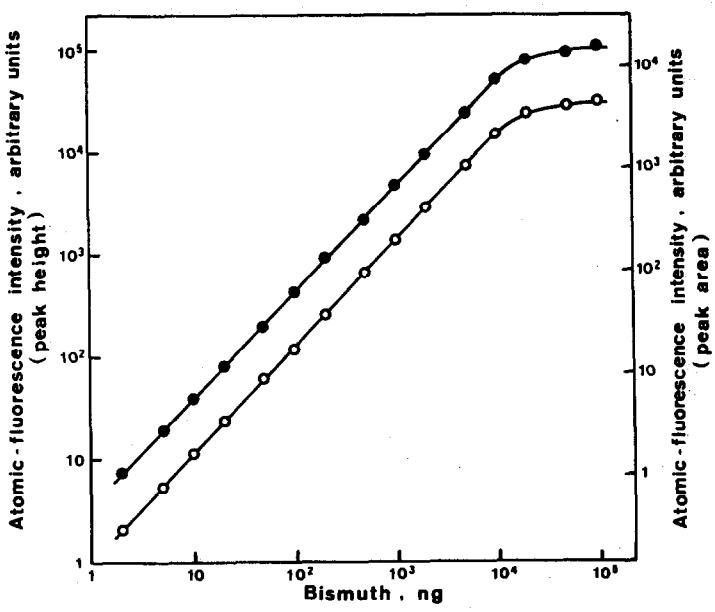

Fig. 3. Analytical working curves for bismuth obtained by peak-height measurement (○) and peak-area measurement (●).

pared bismuth standard solutions. Figure 3 shows the curves simultaneously obtained by the peak-height method and integration method. The peak-area method gave a slightly higher upper limit of linearity. The curves are linear over about four orders of magnitude from the detection limit.

The detection limit, calculated on the basis of a signal-to-noise ratio of 3 as recommended by IUPAC,[36] was 0.1 ng of bismuth, equivalent to 5 pg/ml in a 20-ml sample. Larger samples can be used, with a corresponding improvement in the concentration detection limit. The reagent blank had a value of approximately 2 ng of bismuth in 20 ml of sample volume, however, so the practical detection limit is much higher than the "IUPAC" limit. There was no difference in detection limit between the two methods of measuring the signals.

The fluorescence intensities for standards containing 5, 50, 500 and 5000 ng of bismuth were repeatedly measured simultaneously by the both methods. The results are given in Table 4. The peak-area method gave somewhat better reproducibility.

Effect of acids

The effect of nitric, perchloric, phosphoric and sulphuric acids in the concentration range 0.1–2.0*M* on the fluorescence signals from bismuth solutions in 1.0*M* hydrochloric acid was examined. Except for nitric acid there was little or no effect. Concentrations of nitric acid greater than 1.0*M*, however, caused a depression in the signal. For example, 2.0*M* nitric acid reduced the signal by *ca.* 40%.

Effect of diverse elements

The elements most likely to interfere are those having ions which react with sodium borohydride in acidic media to form a volatile hydride or the element. The interference may result from the alteration of the rate of reaction or co-precipitation of the analyte or both. The elements which form volatile hydrides are those of groups IVA, VA and VIA, and those with ions which are reduced are some of those in groups IB, IIB and VIII. The effect of various elements at the level of 1000-fold ratio to bismuth was first examined. The compounds used were the same as in our previous work.[37,38] The results obtained are shown in Table 5. Interference is deemed to occur when the fluorescence intensity is changed by over ±10% from that for bismuth alone. The following did not interfere: Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Ga, Ge, In, K, La, Li, Mg, Mn, Na, Pb, Rb, Sb, Si, Sr, Th, Tl, V, W, Y, Zn and Zr. In the interference study there was no significant difference between

Table 4. Precision in the measurement of atomic-fluorescence

Bismuth, *ng*	Relative standard deviation*, %	
	Peak-height measurement	Peak-area measurement
5000	3.2	3.0
500	3.5	2.9
50	4.8	3.9
5	6.4	5.9

* Calculated from 10 replicate measurements.

Table 5. Effect of other elements on the bismuth atomic-fluorescence intensity

Element	Compound added	Relative atomic-fluorescence intensity*	Tolerance limit†
Ag	$AgNO_3$	0.15	2
Au	$HAuCl_4$	0.04	0.8
Cu	$Cu(NO_3)_2$	0.54	70
Fe	$FeCl_3$	0.81	800
Mo	$(NH_4)_6Mo_7O_{24}$	0.73	500
Ni	$NiCl_2$	0.05	1.5
Pd	$PdCl_2$	0.02	0.04
Pt	H_2PtCl_6	0.08	0.3
Se	SeO_2	0.09	15
Te	metal in HCl	0.07	20
Hg	metal in HNO_3	1.54	3
Sn	$SnCl_2$	1.20	200

* Relative to 1.00 for the atomic-fluorescence intensity of bismuth alone.
† Ratio [M]/[Bi] found to have no interfering effect.

the peak-area and peak-height methods of measurement. The large depression caused by elements such as Ag, Au, Ni, Pd and Pt is very similar to that in atomic-absorption spectrometry.[23] The enhancement by mercury may be due to simultaneous measurement of the atomic-fluorescence signals from the bismuthine and from the mercury vapour excited by the bismuth EDL, since mercury atomic-fluorescence at 253.7 nm was definitely observed by use of the dispersive system. A trace of mercury was therefore presumed to be trapped in the bismuth EDL from the mercury manometer attached to the vacuum line.[31] With the dispersive system used at the 306.8-nm of bismuth line, mercury at 1000-fold ratio reduced the bismuth atomic-fluorescence intensity by approximately 80%, as in the optical emission spectrometry of bismuth with an inductively coupled plasma combined with a hydride-generation technique.[30]

Finally the tolerance limits were determined and are reported in Table 5. Elimination of interferences was not investigated.

Application to aluminium-base alloys and sulphide ores

For aluminium-base alloys, a 0.5–1.0 g sample was dissolved in 50 ml of 6*M* hydrochloric acid and 2 ml of concentrated nitric acid by gentle heating on a hot-plate. After cooling, the solution was diluted to volume in a 100-ml standard flask with distilled water. This solution was diluted by a factor of 100–600, depending on the bismuth content, with 1.0*M* hydrochloric acid. A 20-ml aliquot was taken for atomic-fluorescence measurement, both the peak-height and peak-area methods being used. The standard additions method was used. The results are shown in Table 6 and are in good agreement with those obtained either by flame atomic-absorption

Table 6. Results for the determination of bismuth in aluminium-base alloys and sulphide ores

	This work*				
	Peak-height measurement		Peak-area measurement		
Sample	Average value, *mg/g*	Relative standard deviation, %	Average value, *mg/g*	Relative standard deviation, %	Other atomic spectrometry, *mg/g*
Aluminium-base alloy					
2011	5.8	2.9	5.7	2.3	5.6†
5052	0.087	4.0	0.085	3.5	0.08–0.1§
6000	4.4	5.3	4.4	3.9	4.3†
Sulphide ore					
A mine ore (Cu conc.)	0.037	2.7	0.039	2.6	0.038–0.044‡
B mine ore (S conc.)	0.068	4.4	0.065	2.9	0.064–0.072‡

* Calculated from 5 replicate determinations.
† Certificate value obtained by flame atomic-absorption spectrometry.
§ Obtained by optical emission spectrometry with an inductively coupled plasma.
‡ Obtained by flame atomic-absorption spectrometry.[39]

Table 7. Experimental conditions for optical emission spectrometry of bismuth with an inductively coupled plasma

Plasma frequency	27.12 MHz
Forward RF power	1.6 kW
Argon coolant gas flow-rate	1.3 l./min
Argon plasma gas flow-rate	0.8 l./min
Argon sample transport gas flow-rate	0.4 l./min
Sample uptake rate	1.0 ml/min
Height of observation zone above work coil	15 mm
Photomultiplier voltage	464 V
Wavelength	306.8 nm
Entrance slit-width	10 μm
Exit slit-width	10 μm
Integration time for measuring the signals	10 sec

spectrometry or optical emission spectrometry with an inductively coupled plasma (Nippon Jarrell-Ash Model ICAP-500, experimental conditions in Table 7).

For sulphide ores, a 2.0–2.5 g sample was dissolved in 50 ml of *aqua regia* (1:1) by gentle heating on a hot-plate. The solution was cooled, 10 ml of 25% ammonium citrate solution were added and the insoluble matter was filtered off. The filtrate was diluted to volume in a 100-ml standard flask with distilled water. The solution was diluted 200-fold with 1.0*M* hydrochloric acid and analysed in the same way as the aluminium-base alloys. The results are given in Table 6 and are in good agreement with those by flame atomic-absorption spectrometry.[39]

CONCLUSIONS

The system described has proved to be highly sensitive and reliable for the determination of bismuth at the nanogram level. The light scattering due to non-volatilized aerosol particles when direct nebulization of solutions is used was markedly reduced by the use of the bismuthine-generation technique, resulting in improvement in signal-to-noise ratio for the bismuth atomic-fluorescence measurement. The use of the bismuth EDL containing bismuth tri-iodide led to a great improvement in sensitivity because the iodine line at 206.16 nm was also available for the excitation of bismuth atoms.

The detection limit and linear dynamic range could be further improved by use of other atomization sources (*e.g.*, heated quartz cell, inductively coupled plasma, *etc.*) instead of a flame, and with a filter (such as a chlorine filter) to reduce flame background noise.[40,41] Experiments are in progress to investigate this possibility. However, the reagent blank is the main factor determining the detection limit.

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SHORT COMMUNICATIONS

DUAL-WAVELENGTH SPECTROPHOTOMETRIC DETERMINATION OF CADMIUM WITH CADION

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Summary—Cadmium has been determined by dual-wavelength spectrophotometry with cadion, *p*-nitrobenzenediazoaminobenzene-*p*-azobenzene, and a non-ionic surfactant, Triton X-100. Cadion and its cadmium chelate are dissolved in a micellar solution of the surfactant. The absorbance difference at the wavelength of maximum absorption of the cadmium chelate (477 nm) and that of cadion (566 nm) is measured. A combination of triethanolamine, iminodiacetate and citrate is very effective for masking other ions. Cadmium in zinc metal can be determined without prior separation.

Cadion, *p*-nitrobenzenediazoaminobenzene-*p*-azobenzene, was first introduced by Dwyer[1] as a highly sensitive reagent for detecting cadmium, which forms a red water-insoluble chelate. Recently cadion has been used for the determination of cadmium by the ring-oven technique.[2] Cadion and its derivatives have also been applied to the spectrophotometric determination of cadmium with gelatin[3] or vinylpyrrolidone[4] as dispersing agent. However, cadmium must be separated from other ions before the determination because of their serious interference.[5,6]

In the present study a combination of triethanolamine (TEA), iminodiacetate (IDA) and citrate was found to be very effective for masking other ions. It was also found that a non-ionic surfactant, Triton X-100, was a good substitute for the dispersing agents. The cadion and its cadmium chelate are dissolved in a micellar solution of the surfactant, so cadion can be used as if it were a water-soluble reagent. Furthermore, the present method is very sensitive. The sensitivity according to Sandell's criterion is half of the previous value for cadion.[3,4] The absorbance difference at the wavelength of maximum absorption of the chelate (477 nm) and that of cadion (566 nm) was measured with a dual-wavelength spectrophotometer (Hitachi Model 356).

EXPERIMENTAL

Reagents

Standard metal-ion solutions. Prepared from high-purity reagents or metals dissolved in 2*M* hydrochloric acid and then diluted as necessary with water.

Cadion solution 0.0125%. Prepared by dissolving 0.0125 g of the compound in a mixture of 20 g of Triton X-100 and 80 g of water.

Masking-reagent solution. TEA, 0.001*M*, sodium iminodiacetate, 0.001*M* and sodium citrate, 0.01*M* adjusted to pH 12 with 0.2*M* sodium hydroxide.

Procedure

A known volume of a standard solution containing less than 2.0 μg of cadmium was taken in a 25-ml standard flask. Then 1 ml of the masking-reagent solution, 1 ml of cadion solution and 2.5 ml of 0.2*M* sodium hydroxide were added successively. The mixture was made up to volume with water and mixed well. The difference in absorbance at 477 and 566 nm, $\Delta_{477-566}$, was determined (1-cm cells) with a full-scale range of 0–0.3.

RESULTS AND DISCUSSION

The absorption spectra of cadion and its cadmium chelate at pH 12.5 are presented in Fig. 1. The absorption peak of cadion is at 566 nm and that of the chelate at 477 nm.

Figure 2 shows the effect of pH, in the presence of the masking reagents, on the absorbance of cadion at 566 nm against water and that of the chelate at 477 nm against a reagent blank. In this case the absorbance was measured with a conventional single-wavelength spectrophotometer. In the pH range 11.5–13.0 the absorbance of the chelate at 477 nm is constant, while that of cadion at 566 nm is constant if the pH is ≥ 12.2. Hence the pH chosen was 12.5 for the determination of cadmium.

Two wavelengths were chosen such that the difference in absorbance was maximal:[7,8] 477 and 566 nm. In common absorption spectroscopy the intensity ratio of light of the same wavelength transmitted or absorbed by a sample and reference material in separate cells is measured. In dual-wavelength spectroscopy, light of two different wavelengths is passed through the same sample and the difference in absorbance is measured. Before this measurement, the bilateral optical attenuators of the dual-wavelength spectrophotometer are adjusted so as to compensate for the intensity difference at the two wavelengths, a reagent-blank, prepared according to the procedure,

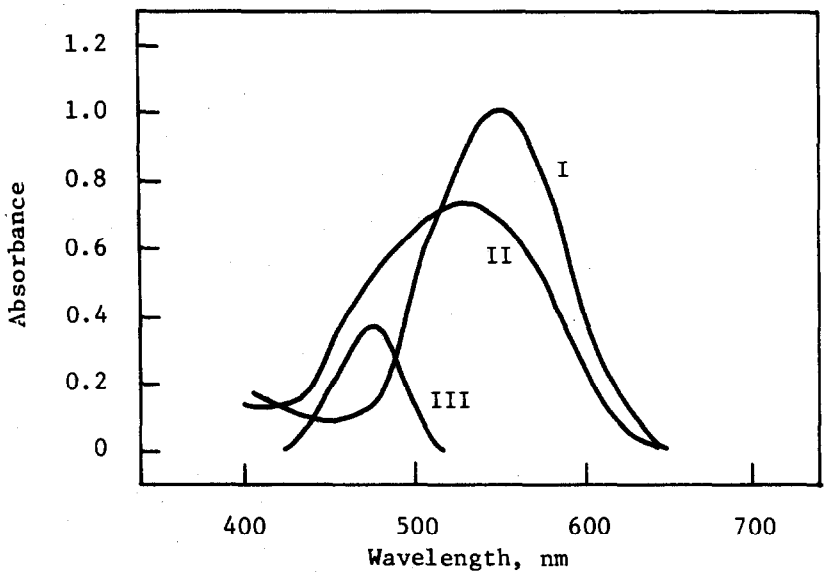

Fig. 1. Absorption spectra of cadion and its cadmium chelate at pH 12.5. I: reagent blank, ref. water; II: Cd(II) 5.00 μg; ref. water; III: Cd(II) 5.00 μg; ref. reagent blank.

being used for this purpose. Thus the absorbance difference at 477 and 566 nm for a sample containing the cadmium chelate, which is expected to form the 1:3 chelate (mole ratio of cadmium to cadion), is measured. It can be expressed as follows:

$$\Delta_{477-566} = (\epsilon^{ML_3}_{477}[ML_3] - 3\epsilon^{L}_{477}[ML_3]) - (\epsilon^{ML_3}_{566}[ML_3] - 3\epsilon^{L}_{566}[ML_3]). \quad (1)$$

To a first approximation, if ϵ^{L}_{477} and $\epsilon^{ML_3}_{566}$ are ignored, equation (1) can be rewritten as equation (2), which will illustrate well the usefulness of dual-wavelength spectroscopy. The first term in equation (2)

$$\Delta_{477-566} = \epsilon^{ML_3}_{477}[ML_3] + 3\epsilon^{L}_{566}[ML_3] \quad (2)$$

gives the increase in the absorbance at 477 nm due to the formation of the chelate, and the second the decrease in the absorbance at 566 nm, due to consumption of cadion consumed for the formation of the chelate. In dual-wavelength spectrophotometry, therefore, three times the decrease in the absorbance of the cadion is added to the increase in the absorbance of the chelate, thus making it possible to increase the sensitivity.

From Fig. 1 ϵ^{L}_{477} and ϵ^{L}_{566} were found to be 1.7×10^4 and 6.7×10^4 l.mole^{-1}.cm^{-1} respectively. On the basis of these values and other results $\epsilon^{ML_3}_{477}$ and $\epsilon^{ML_3}_{566}$ were estimated to be 18.4×10^4 and 1.7×10^4 l.mole^{-1}.cm^{-1} respectively. With these

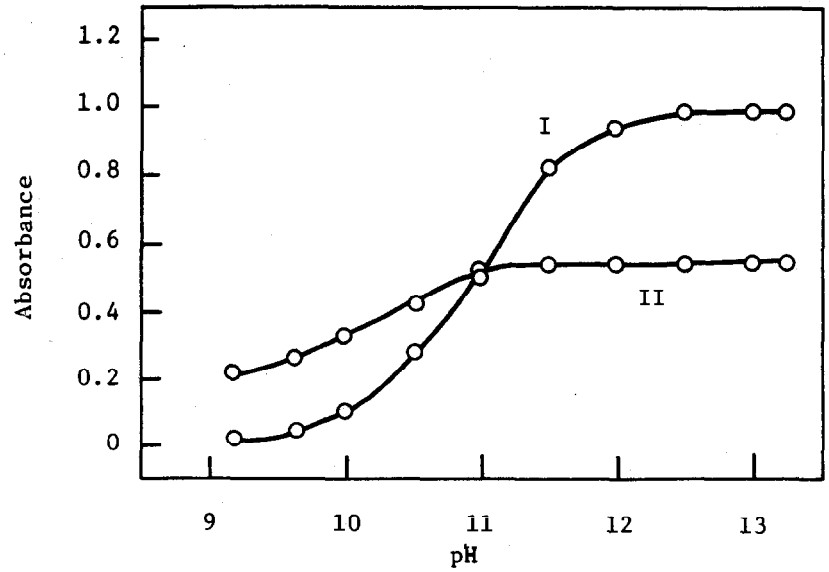

Fig. 2. Effect of pH on the absorbance of cadion at 566 nm and that of the cadmium chelate at 477 nm (1-cm cell). I: cadion; ref. water; II: cadmium chelate, Cd(II) 5.00 μg; ref. reagent blank.

Table 1. Influence of foreign ions on the determination of 0.60 μg of cadmium(II)

Foreign ion	Added, μg	$\Delta_{477-566}$
None	—	0.0754
Fe^{3+}	30	0.0704
Ni^{2+}	10	0.0717
Co^{2+}	50	0.0783
Mg^{2+}	40	0.0730
Mn^{2+}	200	0.0751
Cu^{2+}	500	0.0770
Pb^{2+}	500	0.0732
Ca^{2+}	4×10^3	0.0750
Zn^{2+}	1×10^4	0.0742

Table 2. Average of five determinations of cadmium(II) in zinc metal

Sample* taken, ml		Cd^{2+} added, μg	$(A_{477} - A_{566})$	Cd^{2+} found		Coefficient of variation, %
				μg	μg/g	
A	2	—	0.0930	0.91_4	239	3.8
B	2	1.00	0.1956	1.92_3	241	7.9

* 0.1916 g of zinc metal was dissolved in 3 ml of 6*M* hydrochloric acid and then diluted to 100 ml with water.

numerical values, the sum of the constant factors in equation (1) becomes 31.7×10^4. The apparent molar absorptivity calculated from the slope of a calibration curve prepared according to the procedure was 32.0×10^4. Beer's law is obeyed over the range 0.20–2.00 μg of cadmium(II). The Sandell sensitivity is 0.33 ng/cm^2 for 0.001 absorbance, which is superior to that of other reagents for cadmium except α,β,γ,δ-tetraphenylporphinetrisulphonic acid (0.26 ng/cm^2).[9]

Table 1 shows the influence of other ions on the determination of 0.60 μg of cadmium. When large amounts of zinc, copper(II) and lead are present in the test solution more than 3 ml of 0.2*M* sodium hydroxide should be added to maintain the correct pH. Up to 10 mg of zinc, 0.5 mg of copper(II) and 0.5 mg of lead can be tolerated. These tolerance limits are 10–100-fold higher than those of the cadion methods[3,4] previously reported. Iron and nickel interfere.

As a test of the method cadmium was determined in a sample of zinc metal (analytical grade). A sample solution was prepared by dissolving the zinc metal (0.1916 g) in 3 ml of 6*M* hydrochloric acid and diluting to 100 ml with water. To check the recovery of cadmium a 2-ml aliquot of the sample solution was analysed both alone and when spiked with 1.00 μg of cadmium(II). The average of five determinations and the coefficient of variation are presented in Table 2. The results show that the present method is apparently satisfactory.

CONCLUSION

A selective and sensitive method for the spectrophotometric determination of cadmium has been developed. Although many spectrophotometric methods for cadmium have been reported, most of them require prior separation of the cadmium. The interference of zinc is generally serious. Since the use of TEA, IDA and citrate is very effective for masking other ions, the present method will provide a simple means for the determination of amounts of cadmium from several micrograms down to fractions of a microgram.

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A NEW SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF FORMALDEHYDE IN AIR

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Summary—A new spectrophotometric method for the determination of formaldehyde is described, based on a colour reaction with oxalyldihydrazide and copper(II). The optimum reaction conditions, and other analytical parameters such as interferences, Beer's law, sensitivity, collection efficiency, *etc.* have been studied.

Aldehydes are considered to be one of the major pollutant groups present in air, as they are very irritative to skin, eyes and mucous membranes.[1] The principal source of aldehydes in the free atmosphere is the partial oxidation of organic matter and fuel. Aldehydes are also present at various work sites, where they are used as a raw material.[1,2] Various methods have been reported for determining aliphatic aldehydes in the atmosphere[3–8] and in most of them the aliphatic aldehydes are reported as formaldehyde, owing to its stability and predominance in the polluted atmosphere.[9,10] The present work describes a new spectrophotometric method for determination of formaldehyde, based on a sensitive colour reaction with oxalyldihydrazide (ODH) and copper(II). A blue water-soluble complex is formed. The optimum reaction conditions and other analytical parameters of the colour reaction have been investigated. The proposed method is simple and reasonably sensitive.[5,7]

EXPERIMENTAL

Reagents

Standard formaldehyde solution. Prepared by diluting 1 ml of 38–40% formaldehyde solution to 250 ml, standardizing titrimetrically,[11] and diluting to give a standard solution containing 20 μg of formaldehyde per ml.

Saturated oxalyldihydrazide (ODH) solution. The reagent was prepared by the addition of hydrazine hydrate (0.1 mole, dissolved in alcohol) to diethyl oxalate (0.05 mole in alcohol). The white solid obtained was crystallized from water (m.p. 238–239°).

Copper(II) solution, $1 \times 10^{-3} M$. Prepared by dissolving metallic copper in nitric acid [other cupric salts can also be used].

Ammonium acetate solution, 20%.

All chemicals used were of analytical reagent grade.

Procedure

An absorption solution was prepared by mixing 10 ml of ODH solution and 5 ml of ammonium acetate solution and divided between 2 impingers of 35 ml capacity, which were then connected in series to a source of suction. Air was drawn through the absorption solution at not more than 1.5 l./min. After the sampling, the solutions were quantitatively transferred to a 25-ml standard flask. After 5 min 0.6 ml of copper(II) solution was added and 10 min later 1.4 ml of copper(II) solution was added and the solution made up to the mark. The absorbance of the blue colour developed was measured at 620 nm, 25 min after the final reagent addition, against a reagent blank prepared under the same conditions. The amount of formaldehyde was deduced from a calibration curve prepared in the same manner and covering the range 15–90 μg/25 ml.

RESULTS AND DISCUSSION

Spectral characteristics

The formaldehyde-ODH reaction product forms a blue complex with copper(II). The absorption spectrum is shown in Fig. 1. The complex exhibits maximum absorption at 615–625 nm. The blank absorption is negligible in this region, so for all practical purposes distilled water can be used as reference. All subsequent studies were carried out at 620 nm.

Effect of experimental conditions

The absorbance was found to be maximal and unaffected by pH in the range 5.6–6.8. Hence 5 ml of 20% ammonium acetate solution were used for adjusting the pH in further studies.

The effect of ODH was studied by taking various molar ratios of the reagent and formaldehyde and developing the colour as recommended in the procedure. The maximum absorbance was obtained at an ODH:HCHO ratio of 4:1 and remained constant at higher ratios. However, lower ODH concentrations cause instability of the colour, hence, a saturated solution of oxalyldihydrazide in water was used for all experimental work.

Maximal absorbance was obtained with a Cu(II):HCHO ratio between 1:2 and 3:1. At higher ratios turbidity occurs. It was also found that addition of the copper(II) in one lot causes low results at lower concentrations of formaldehyde. This behaviour was reported earlier, in a different connection, by Jacobson *et al.*[12] However, if the copper(II) is added in two lots, with an interval between them, good results are obtained.

The amount of ammonium acetate is not very significant but its absence cause slow colour development. It provides the pH required for colour development and checks precipitation of lead, zinc, cadmium

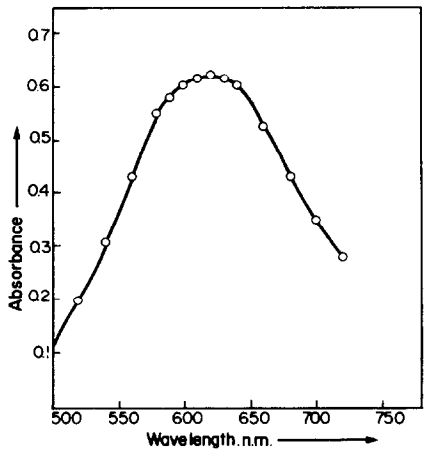

Fig. 1. Absorption spectrum of formaldehyde–oxalhydihydrazide–copper(II) complex in water. HCHO = 60 μg/25 ml.

and mercury(II). Maximum absorbance is attained 25 min after the final reagent addition and is stable for up to 180 min, then starts decreasing.

The colour system is found to obey Beer's law at 620 nm from 15 to 90 μg of formaldehyde in 25 ml. The optimal concentration evaluated from a Ringbom curve[13] is 20–70 μg/25 ml. The molar absorptivity is $7.70 \pm 0.05 \times 10^3$ l.mole^{-1}.cm^{-1}.

Effect of other species

The effect of 20 foreign species on the formaldehyde determination was studied by adding the species in question to a solution containing 0.03 mg of formaldehyde, and applying the procedure. The tolerance limits are tabulated in Table 1. Sulphur-bearing compounds interfere. Other aliphatic aldehydes also give the colour reaction, but the wavelengths of maximum absorption and the molar absorptivities differ.

Collection efficiency

A modification of Wilson's procedure[9] was used for investigating the collection efficiency of the absorption solution. Purified air was passed through a formaldehyde-evaporation chamber, preheated to 60–70°. Known amounts of formaldehyde were evaporated from the chamber and absorbed in the solution; 95–96% absorption was achieved by using 2 impingers with 7.5 ml of absorption solution in each, at a flow-rate of 1.5 l./min.

Composition of the complex

The composition of the complex was determined by Job's method.[14] The results indicate a reacting ratio of 2:2:1 for formaldehyde:ODH:Cu(II), which would agree with Nilsson's postulate[15] of *in situ* formation of an oxalydihydrazone which can then hydrolyse to form the monohydrazone and its blue copper complex.

The present method is very simple and the reagents are readily available in high purity. The 95–96% collection efficiency is the one of the main advantages of the method. The method has a high tolerance limit for aniline, phenol and urea, which are the expected co-pollutants from various industries such as the resin industry.

Table 1. Tolerance limits in the determination of 0.03 mg of HCHO in 25 ml

Species added	Tolerance limit *mg*
Aniline	45
Benzene	60
Toluene	60
Formic acid	40
Acetic acid	40
Nitrobenzene	30
Ethanol	50
Phenol	30
Urea	30
Methylamine	5
Carbon disulphide	Interferes
Nitrogen dioxide	1
[a]Nitrogen dioxide	3
Sulphur dioxide	0.015
Carbon dioxide	25
Hydrogen sulphide	Interferes
[b]Pb^{2+}	0.5
[b]Cd^{2+}	0.5
[b]Zn^{2+}	0.5
[b]Hg^{2+}	0.5
Ammonia	25

[a] In the presence of 2 ml of 2% sodium azide.
[b] Higher concentrations yield precipitation.

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RAPID X-RAY FLUORESCENCE ANALYSIS OF TRACE METALS COLLECTED BY USING NAPHTHALENE POWDER DOPED WITH 1-(2-THIAZOLYLAZO)-2-NAPHTHOL

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Summary—Naphthalene powder doped with 1-(2-thiazolylazo)-2-naphthol is used as collector for traces of metals, which are then determined by X-ray fluorescence analysis of the naphthalene. The method is used for traces of nickel.

One of us has already proposed a method of extracting metal ions from aqueous solutions with an oxine-doped naphthalene pellet,[1] depending on the fact that naphthalene melts at 80°. The method has been applied to trace analysis for various metal ions.[2,3] In the present study, it was found that metal ions can be gathered with naphthalene powder doped with 1-(2-thiazolylazo)-2-naphthol (TAN) from aqueous solutions at room temperature. The naphthalene is then pressed into a disk, which is examined by X-ray fluorescence. The new method is applied to determination of traces of nickel.

EXPERIMENTAL

Reagents

A nickel solution was prepared by dissolving nickel chloride (analytical grade) in 0.1*M* hydrochloric acid. TAN, naphthalene and other reagents used were of analytical grade. A buffer solution of pH 6.9 was prepared from ammonia and ammonium dihydrogen phosphate.

Preparation of TAN-doped naphthalene powder

TAN (0.050 g), naphthalene (25.00 g) and 200 ml of distilled water were warmed in a 500-ml Erlenmeyer flask on a water-bath to melt the naphthalene completely, and then shaken vigorously. When the mixture is cooled to room temperature, the naphthalene solidifies to form granules. The granules, TAN-doped naphthalene, are filtered off on paper, dried, and finally crushed into powder with an agate mortar. A 2.00-g portion of this powder is used to collect metal ions from aqueous solutions.

Separation and determination of nickel

Place the nickel solution (containing <18.0 μg of nickel) in a 50-ml Erlenmeyer flask. Add 5 ml of pH 6.9 buffer solution and then dilute to *ca.* 40 ml with distilled water. Add 2.00 g of TAN-doped naphthalene powder to the solution and stir the mixture for 45 min at room temperature, to collect the nickel. Filter off the powder and wash it with a small amount of distilled water. Dry the powder at room temperature. Transfer 1.50 g of the dried powder into an aluminium ring (5 mm thick and 43 mm in diameter) placed on a stainless-steel plate. Press the powder at 25 tons to prepare a disk. Measure the intensity of the $K\alpha$ line emitted from the nickel in the disk.

RESULTS AND DISCUSSION

A 10.0-μg amount of nickel was recovered quantitatively from up to 200 ml of aqueous solution. No nickel could be detected in the residual aqueous phase. A calibration graph was linear in the range from 0 to 18.0 μg of nickel (in 40 ml of sample solution). The main advantage of this method is that the preparation of TAN-doped naphthalene powder is quite simple. This method can be applied in the same manner to the determination of metal ions other than nickel since TAN is a rather non-specific reagent; other chelating agents may also be used in a similar way. The method should be suitable for water analysis since the metal ions concerned are easily separated and concentrated onto the naphthalene powder doped with chelating agent; the powder can be used in the field for collection of the metal ions, and then analysed in the laboratory. The optimum pH for reaction of TAN with nickel is 6.9.[4,5] The method has been applied to determination of nickel,[6] zinc[7] and cobalt[7] and is also applicable for copper and manganese.

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DETERMINATION OF CARBOHYDRATES BY DIRECT INJECTION ENTHALPIMETRY

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Summary—An analytical method for the determination of carbohydrates is described, which is based on the enthalpimetric signal obtained at the beginning of the reaction with periodate. The apparatus is described and relevant aspects of the procedure are discussed. Single carbohydrates can be determined in a few minutes with a precision of 1%. Analysis of mixtures of glucose and fructose is reported.

Determination of carbohydrates is mainly based on their reducing properties, and frequently involves colour measurements. A common method of assay make use of the oxidation with periodate, the excess of which is determined by addition of potassium iodide and thiosulphate titration of the iodine liberated or by reduction with arsenite followed by titration of the arsenite excess with iodine. These methods, as well as those involving oxidation by copper ions, are subject to various shortcomings[1–3] and satisfactory results are obtained only by use of strictly observed conditions.[3]

Many industrial products containing carbohydrates are coloured because of partial caramelization or the presence of food additives. For these samples optical methods may be subject to error and for this reason thermometric methods of assay have been suggested, in which the excess of periodate is titrated with hydrazine sulphate[4] or mannitol.[5]

In the thermometric or enthalpimetric methods, it would be advantageous to use the periodate oxidation reaction directly. Although there is a favourable enthalpy change, the rate of the overall reaction is too slow for practical applications. However, under certain conditions, the first stage of the reaction is fast whereas the following one is slow. In these circumstances the measurements can be done during a time when the fast portion of the reaction is substantially complete, but the slow step has still scarcely begun. This is the basis of the analytical method described in this report.

EXPERIMENTAL

Apparatus

The apparatus consisted of a reaction cell, a Wheatstone bridge (Leads & Northrup, cat. number 4760) and a strip-chart recorder (Servogor S, model RE541). The reaction cell, shown in Fig. 1, is a 100-ml Dewar flask which contains the thermistor probe, a magnetic stirring bar and a spiral made of polyethylene tube of about 2 mm outside diameter. The length of this tube is about 1 m and it is held in the spiral form with Teflon strips. The syringe (or pipette) connection to the spiral is made of polyethylene tube of larger diameter. The thermistor used had a nominal resistance of 2200 ohms at 25°. A Dewar-type closure is used.

Reagents

Reagent-grade chemicals were used throughout. The sodium periodate solution was prepared by weighing 7.353 g of $HIO_4.2H_2O$, adding 22.5 ml of 0.960*M* sodium hydroxide and diluting to 50 ml. Phosphate buffer, containing 4.00 g of $NH_4H_2PO_4$ and 17.57 g of $(NH_4)_2HPO_4$ per litre, was used for determinations at pH 7.2.

Procedure

Buffer solution (50 ml) is placed in the reaction cell. A sample containing up to 25 mg of carbohydrate is dissolved in the buffer solution, with the total volume being equal to 55 ml. With a pipette, 2 ml of periodate solution are put into the polyethylene-tube spiral, and this is immersed in the Dewar, as shown in Fig. 1. The Dewar is

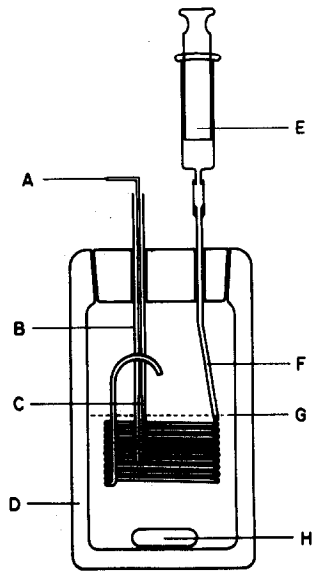

Fig. 1. Reaction cell; (A) thermistor leads; (B) glass tube; (C) thermistor immersed in mineral oil; (D) Dewar flask; (E) syringe; (F) polyethylene tube; (G) solution level; (H) magnetic stirring bar.

closed and the baseline is recorded during 3–5 min. Air is injected into the spiral by depressing the syringe, so that the periodate solution is expelled. The enthalpogram is recorded and the deflection is read at a chosen time, varying from 2 to 5 min. The carbohydrate concentration is calculated by using the equation obtained from the calibration points.

RESULTS AND DISCUSSION

Heat of dilution and initial temperature difference

A major drawback of enthalpimetric analysis is the influence of heat effects due to dilution and to the initial temperature difference between the two reacting solutions. This last effect may become serious. Simple calculations[6] show that a significant error in the determinations may be caused by a difference of only 0.2° between the initial temperatures of the periodate and carbohydrate solutions. It is for this reason that in the enthalpimetric method of determination of α-diols proposed by Jeffries and Fresco,[7] the reacting solutions were allowed to stand overnight for temperature equilibration. In our work the problem has been solved by placing the periodate solution inside the spiral which is immersed in the carbohydrate solution. Owing to the large contact area, temperature equilibrium is reached almost instantaneously, as can be seen from the behaviour of the recorded baseline.

The dilution of sodium periodate in the buffer solution (pH = 7.2) was found to be exothermic and the heat evolved equal to about 40% of the average signal measured. Although calibration curves could be used which take this effect into account, it certainly introduces a great source of uncertainty. However, in the same buffer, the dilution of periodic acid is endothermic and of comparable magnitude. A solution obtained by partial neutralization of periodic acid (see experimental section) was found to have virtually no heat of dilution and was, therefore, chosen for use in our procedure.

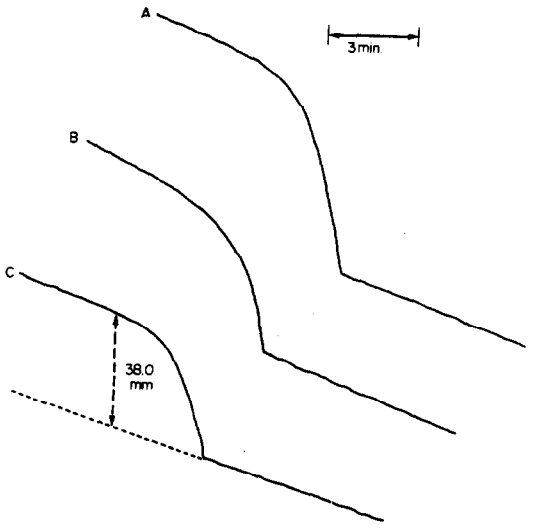

Fig. 2. Typical enthalpograms. (A) 12.5 mg of arabinose; (B) 10.0 mg of fructose; (C) 7.5 mg of xylose.

Determination of single carbohydrates

The influence of acidity on the rate of reaction and on the magnitude of the signal was studied in the pH range from 1 to 10. Several experiments were performed, mainly with fructose and glucose, using different buffer solutions and an excess of periodate. The results agreed with the general description in the literature[8] for this reaction. The optimum pH for the determination of single carbohydrates was found to be around 7.2. At this pH the first stage of the reaction is fast and the following step is very slow. Also, the magnitude of the ΔT obtained is more favourable.

Figure 2 shows typical enthalpograms and gives an example of the deflection measurements. The time chosen for the measurements varies from 2 to 5 min, being smaller for carbohydrates which react faster. Under the experimental conditions used, a chart deflection of 1 mm corresponded to a temperature change of 0.0026°, estimated[9] from the thermistor parameters.

The calibration curves were linear for all carbohydrates and passed through the origin. This is what is expected for reactions which follow pseudo-first-order kinetics, as seems to be the case here. It is believed that the first exothermic stage of the reaction represents consumption of one or more moles of periodate per mole of sugar. It is interesting to note that the slope of the calibration curve for ribose (1.3 mm/mg) was much smaller than for the other sugars (3.6–4.8 mm/mg). This fact probably reflects formation of the rather stable complex[10] of ribose with periodate.

Determination of known samples of carbohydrates by the proposed method yielded the results given in Table 1. The amounts found were calculated by reading the enthalpogram deflections and substituting them in the equations obtained by linear regression analysis of the calibration points. Each concentration is the mean of three runs. The average uncertainty of the determinations, as shown by Table 1, is less than 1%. This seems to be quite good precision, especially considering that the determination can be completed within a few minutes. About the same dependability is reported by Bark and Prachuabpaibul[4] and Bark and Edwards[5] for thermometric

Table 1. Results obtained for different carbohydrates

Compound	Amount taken, *mg*	Amount found, *mg*	Relative error, %
Arabinose	12.50	12.66	+1.3
Fructose	7.50	7.43	−0.9
Galactose	12.00	12.20	+1.7
Glucose	2.50	2.49	−0.4
Ribose	17.50	17.55	+0.3
Xylose	13.50	13.41	−0.7

methods of determination of carbohydrates. The procedure proposed in this report is, however, simpler and faster.

Mixtures of glucose and fructose

Analysis of mixtures of glucose and fructose is important because of their common occurrence in nature. In some cases, such as in the analysis of molasses, it is sufficient to have a knowledge of the total sugar content. It was found that the enthalpimetric signals given by glucose and fructose at pH = 7.2, when read at a time equal to 2.5 min, were about the same. The enthalpograms gave calibration points which fitted straight-line equations almost perfectly (correlation coefficients 0.9998). The slope for glucose was 3.58 mm/mg and that for fructose was 3.60 mm/mg. The difference is well within the experimental error and therefore the ΔT obtained for the mixture should be a function of the total sugar content. Experiments with mixtures of glucose and fructose confirmed that the enthalpimetric signal is a reliable indication of the total sugar present.

The simultaneous determination of glucose and fructose was attempted by using the technique of kinetic analysis. The largest ratio (equal to 3) of the pseudo-first-order rate constants was found at pH = 5.2 (acetate buffer) and this medium was used for the determinations. The calculations were performed by using the method of proportional equations[11] and the times chosen for the measurements were 1 and 3 min. For mixtures of equal amounts of glucose and fructose the precision and accuracy were around 4%, but the uncertainty increased rapidly as the ratio of concentrations departed from unity. However, procedures which involve the hydrolysis of saccharose give mixtures containing comparable amounts of these two reducing sugars. For such samples this method may find application, because of its simplicity, great rapidity and ease of automation.

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EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF NICKEL WITH 2-HYDROXYACETOPHENONE OXIME AND SIMULTANEOUS DETERMINATION OF COPPER AND NICKEL

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Summary—It is observed that 2-hydroxyacetophenone oxime can be used for the quantitative extraction of nickel in the pH range 6.6–7.8 into methyl isobutyl ketone. The organic layer shows maximum absorbance at 375 nm. Beer's law is obeyed over the range 1–6 ppm. The colour of the organic layer is stable for more than 48 hr. Interferences have been studied and methods are suggested for their elimination. Copper and nickel are both quantitatively extracted at pH 7 and can be determined simultaneously and accurately in the range 1–6 μg/ml for copper and 1–4 μg/ml for nickel.

2-Hydroxyacetophenone oxime (HAO) has been used as a gravimetric reagent for the determination of copper, nickel and palladium.[1] Poddar also used it for the spectrophotometric determination of uranium[2] and vanadium.[3] We have now examined its use as an extraction reagent. The extraction and photometric determination of copper have already been reported.[4] It is now shown that nickel can be similarly determined.

EXPERIMENTAL

Reagents

HAO was prepared from 2-hydroxyacetophenone by the usual procedure,[5] and a 1.5% solution in 50% aqueous methanol was used. Stock 0.1*M* solutions of ammonium nickel sulphate and copper sulphate were prepared in conductivity water and standardized gravimetrically with dimethylglyoxime[6] and titrimetrically[7] respectively. The stock solutions were diluted as required.

General procedure

A portion of solution (containing 10–60 μg of nickel) and 1 ml of the reagent solution were taken in a 25-ml separatory funnel and diluted to 15 ml with ammonia–ammonium chloride buffer (pH 7), and shaken vigorously with 10 ml of MIBK for about 3 min, then allowed to stand for 5 min for the layers to separate. The green organic layer was removed, dried over anhydrous sodium sulphate and measured spectrophotometrically at 375 nm against a reagent blank.

Procedure for simultaneous determination

A known volume of the solution containing copper and nickel is treated in the same way as a nickel solution, except that the MIBK/aqueous phase mixture is shaken for 5 min instead of only 2, and the absorbance is measured at 355 and 375 nm.

RESULTS AND DISCUSSION

The absorption spectrum of the organic layer has a maximum at 375 nm (Fig. 1). At this wavelength the reagent shows negligible absorbance. Beer's law is obeyed in the nickel concentration range 1–6 μg/ml in the organic phase. The molar absorptivity is $(4.1 \pm 0.1) \times 10^3$ l.mole^{-1}.cm^{-1}. The absorbance is constant for up to 48 hr.

Variation of the pH from 1.0 to 10.0 (Fig. 2) shows that there is no extraction at pH below 4.5. Quantitative extraction is achieved in the pH range 6.6–7.8. Of the various organic solvents tried, only chloroform and MIBK were found to extract the complex quantitatively. MIBK was chosen because its volatility is less than that of chloroform. For complete extraction the reagent concentration must be at least 60 times the metal concentration. Variation of the shaking time from 1 to 5 min shows that extraction is quantitative after 2 min of shaking.

Various ions were examined for their effect on the determination of nickel. The tolerance limit was taken

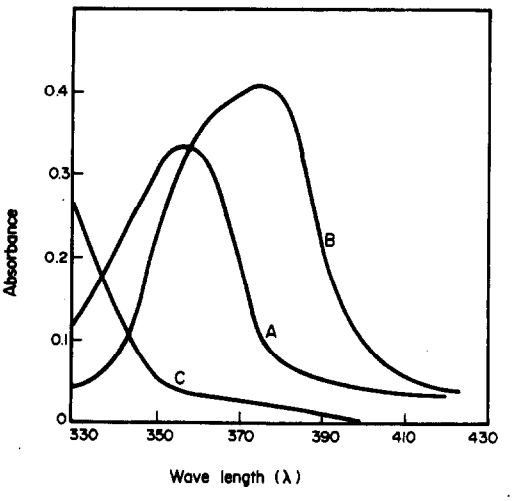

Fig. 1. Absorption spectra: A = Cu(II)–OHAPO complex against reagent blank; B = Ni(II)–OHAPO complex against reagent blank; C = Reagent blank against MIBK; Cu(II) = $1 \times 10^{-4}M$; Ni(II) = $1 \times 10^{-4}M$; OHAPO = $1 \times 10^{-2}M$.

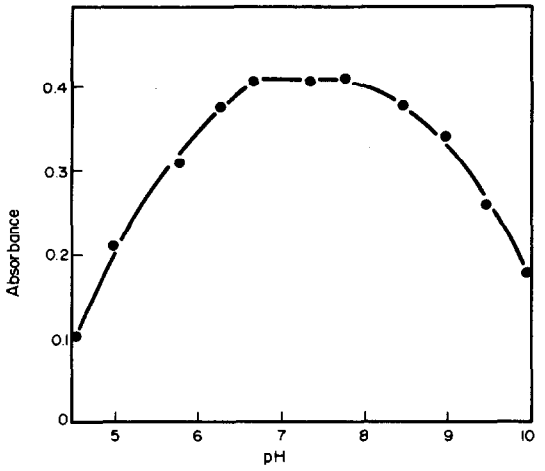

Fig. 2. Absorbance of extracted Ni(II)–OHAPO as a function of pH; Ni(II) = $1 \times 10^{-4}M$; OHAPO = $1 \times 10^{-2}M$.

Table 1. Tolerance limit for various ions in the determination of 35 μg of Ni by extraction at pH 7.0

Tolerance limit, μg	Foreign ion
5×10^4	Sr^{2+}, Na^+, ClO_4^-
1×10^4	Mg^{2+}, Ca^{2+}, Ba^{2+}, K^+, V^{5+}, Mo^{6+}, W^{6+}, Cd^{2+}
1×10^4	CH_3COO^-, $S_2O_3^{2-}$, Br^-, F^-, Cl^-, PO_4^{3-}, CO_3^{2-}, NO_3^-, tartrate
5×10^3	Pb^{2+}, SCN^-, AsO_3^{3-}
2×10^3	Sn^{2+}, Ag^+
1×10^3	Zn^{2+}, Bi^{3+}, $C_2O_4^{2-}$
5×10^2	Citrate
1×10^2	UO_2^{2+}, Ce^{4+}, Cr^{3+}

Table 2. Simultaneous determination of copper and nickel

Taken, μg		Found, μg		Error %	
Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}
55.6	23.5	57.0	23.7	2.6	0.7
47.7	35.2	47.6	35.1	—	0.5
47.7	29.4	48.0	30.0	0.8	2.6
47.7	23.5	48.1	24.2	0.9	3.2
47.7	17.6	47.8	17.9	0.3	1.4
55.6	29.4	55.2	29.8	0.8	1.5
39.9	29.4	40.5	29.6	1.5	0.9
31.8	29.4	31.5	29.4	0.9	—

Table 3. Determination of copper and nickel in German silver

	Amount taken, μg		Amount found, μg		Error %	
Sample	Cu	Ni	Cu	Ni	Cu	Ni
1	48.1	18.6	47.7	18.4	0.8	1.2
2	56.1	21.7	55.5	21.5	1.1	1.3

* From analysis by standard methods.[9]

as the amount (μg) of the foreign ion required to cause 2% error in the absorbance of the organic layer. The results are presented in Table 1. Cobalt interferes seriously and must first be separated by extraction with thiocyanate into isoamyl alcohol. This treatment does not affect the nickel. Zr^{4+}, Th^{4+}, Al^{3+} are precipitated and Fe^{3+} interferes by forming a coloured complex. However, thorium, zirconium, aluminium and amounts of iron less than 100 μg can be masked with fluoride. Larger amounts of iron and Cr^{3+} must be removed before extraction of nickel. This is achieved by extraction with mesityl oxide.[8] EDTA prevents the colour reactions with HAO.

Simultaneous determination of copper and nickel

Both copper and nickel are extracted quantitatively into MIBK at pH 7.0. The organic layer shows two absorption maxima at 355 and 375 nm corresponding to copper and nickel respectively, but the individual peaks overlap considerably. The absorbances of the two complexes are additive at both 355 and 375 nm, so can be used for simultaneous determination of the two metals, the amounts of the two metals in the 10 ml of organic phase being found by solving the necessary equations:

$$\text{Ni} = \left(\frac{A_{375}\epsilon^{Cu}_{355} - A_{355}\epsilon^{Cu}_{375}}{\epsilon^{Ni}_{375}\epsilon^{Cu}_{355} - \epsilon^{Ni}_{355}\epsilon^{Cu}_{375}} \right) \times 0.587\,\text{g}$$

$$\text{Cu} = \left(\frac{A_{355}\epsilon^{Ni}_{375} - A_{375}\epsilon^{Ni}_{355}}{\epsilon^{Ni}_{375}\epsilon^{Cu}_{355} - \epsilon^{Ni}_{355}\epsilon^{Cu}_{375}} \right) \times 0.635\,\text{g}$$

where A_{355} and A_{375} are the absorbances at 355 and 375 nm and the ϵ values are the molar absorptivities for the nickel and copper complexes at these wavelengths.

Typical results for synthetic mixtures are given in Table 2 and for German silver in Table 3. Nickel can be determined in 20 min.

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PREPARATION AND PROPERTIES OF A CHELATING RESIN CONTAINING THE NITROSORESORCINOL GROUP

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Summary—A macroreticular polystyrene-based chelating resin with the nitrosoresorcinol group as the functional group has been synthesized. The resin shows selectivity for copper(II), iron(III), and cobalt(II). The sorption behaviour of cobalt(II) is examined in detail, with the intention of using the resin analytically. Iron(III) and cobalt(II) are separated in a column operation by stepwise elution with oxalic acid solution and hydrochloric acid respectively.

Since 1-nitroso-2-naphthol was first used for the separation of cobalt from nickel by Ilinski and von Knorre,[1] this reagent has been widely utilized in inorganic analysis, mainly as a reagent for cobalt. It is well known that some analogous compounds containing adjacent nitroso and hydroxyl (phenolic) groups form complexes with a number of metal ions, such as cobalt(II, III), copper(II), iron(II, III), nickel(II), and palladium(II).[2]

The incorporation of these functional groups into a polymer matrix is of interest in connection with trace concentration and separation of heavy metal ions. Previously, Eccles and Vernon[3] have synthesized a macroreticular chelating resin containing 4-(2-pyridylazo)resorcinol, and studied its properties with nine metal ions. They suggested that the nitroso group produced from the azo group and phenol group in the resin would appear to play an important role in the sorption of metal ions. This paper describes the preparation and metal-sorption behaviour of a macroreticular resin containing the nitrosoresorcinol group.

EXPERIMENTAL

Apparatus and reagents

Infrared spectra (KBr disks) were recorded with a JASCO DS-701G spectrophotometer. Radioactivity was measured with a single-channel spectrometer equipped with an NaI detector (Aloka Co., Ltd. Models TDC-5U and NDW-351). The stock metal-ion solutions were prepared by dissolving reagent grade nitrates and chlorides in water or approximately 0.1–0.5*M*, acid and were then standardized by titration with EDTA. The radioisotopes, ^{59}Fe and ^{69}Co (as the chlorides in hydrochloric acid solution) were supplied by the New England Nuclear Corp. and the Radiochemical Centre, and were used as tracers.

Preparation of resin

Resin II. To 50 g of resin **I**[4] (chloromethylated styrene–divinylbenzene copolymer, 7.5% divinylbenzene, Cl; 19.3%), 200 ml of dioxan were added and the mixture was stirred for 1 hr at room temperature to allow swelling. To this suspension 45 g of resorcinol and 25 g of powdered anhydrous zinc chloride (freshly fused) were added. Then the mixture was heated to 105–110° and kept at this temperature for 10 hr, with stirring. The product was filtered off, and washed with methanol, 10% hydrochloric acid, water and methanol, successively. After drying in a vacuum desiccator, 57.4 g of light brown resin were obtained.

Resin III. To 500 ml of 1*M* sodium hydroxide containing 22 g of sodium nitrite, 55 g of resin **II** were added, and the suspension was stirred for 1 hr. After cooling to 0°, 33 ml of 38% sulphuric acid were added dropwise to the mixture at 0–5° with stirring. After addition of the sulphuric acid, the stirring was continued at 5° for 2 hr more. The reaction product was filtered off and washed with water and methanol. A brown resin (62 g), which contained 2.9% of nitrogen and 1.1% of chlorine, was obtained.

Sorption of metal ions

Experimental conditions were the same as described in the previous paper.[5]

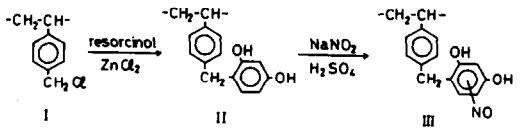
Separation of iron(III) and cobalt(II) by column operation

A glass column was filled with 5 g of resin **III** (1.0 × 15.5 cm). After conditioning with 30 bed-volumes of acetate buffer (0.25*M*, pH 4.0), 2 ml of sample solution, which contained 1 μmole each of ferric chloride and cobaltous chloride, together with the radioisotope tracers, in the acetate buffer, was fed into the column. The column was then washed with the acetate buffer at a flow-rate of 2.5 ml/min, and the iron(III) retained was eluted with 35 ml of 0.01*M* oxalic acid, then 3*M* hydrochloric acid was used for the elution of cobalt(II). The metal contents in the effluents were determined by γ-counting.

RESULTS AND DISCUSSION

Preparation and stability of resin

The resin presented in this study was synthesized from 35–100-mesh chloromethylated styrene–divinylbenzene beads (divinylbenzene 7.5%)[4] through the steps of the reaction shown in Scheme 1. Figure 1 shows the infrared spectra of resins **II** and **III**. A characteristic feature in the spectrum of **III** was the presence of bands corresponding to the nitroso group, at 950, 1350 and 1410 cm^{-1}, and a band at 1600–1700 cm^{-1} due to the tautomeric oxime group.



Scheme 1.

The nitrogen content and hydrogen–sodium exchange-capacity of resin **III** were 2.09 mmole/g and 4.41 meq/g, respectively, whereas the calculated values based on the chlorine content of resin **I** were 3.5 mmole/g for the nitrogen content and 7.0 meq/g for the hydrogen–sodium exchange-capacity. Therefore, we estimated the yield of resin **III** was about 60%.

In order to examine its stability, resin **III** was shaken with 0.1–3*M* hydrochloric acid and 0.1–2*M* sodium hydroxide at room temperature for 4 days. No significant change in the infrared spectra and no decrease in the nigrogen content of resin **III** were observed after the treatment with the acid and alkaline solutions.

When hydroquinone was used in the reaction illustrated in Scheme 1, nitrosation of the hydroquinone resin[6] (which has a similar structure to resin **II**) was unsuccessful because of oxidation of the hydroquinone group with the nitrous acid.[7]

Sorption of metal ions

The sorption of eight metal ions on resin **III** at different pH values is shown in Fig. 2; that of iron(III), copper(II), and cobalt(II) is characteristic. On the other hand, resin **II**, which has no nitroso group, shows no affinity for these ions under the same conditions. Although the affinity of resin **III** for cobalt(II) is not so strong as that for iron(III) and copper(II), the selectivity for cobalt(II) at pH 3–5 is of interest because few resins[3,8,9] are known which have selectivity for cobalt(II) in acidic media, and the sorption of cobalt(II) was therefore examined in detail.

The rate of sorption was determined for cobalt(II) at pH 4.0 by batch operation, with both the hydrogen- and sodium-form of resin **III**. In the case of the sodium-form, the sorption is relatively rapid, and

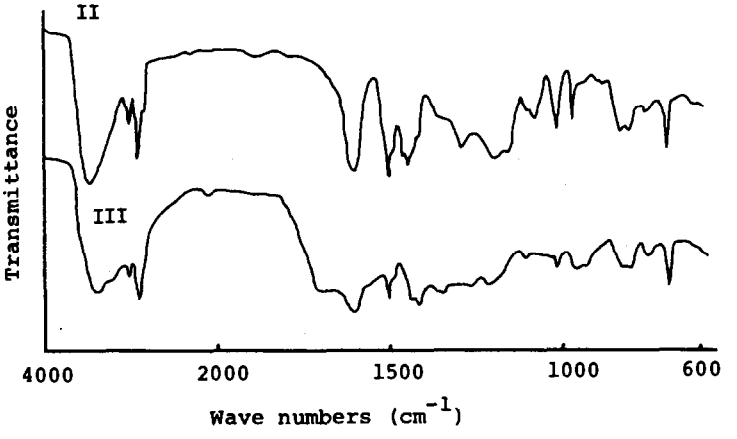


Fig. 1. Infrared spectra of resins in KBr disks.

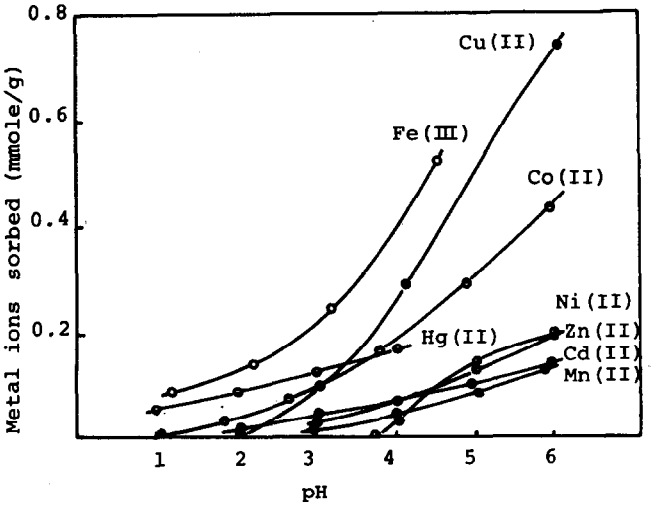


Fig. 2. Effect of pH on sorption of metal ions. Shaking time 24 hr; resin **III** 100 mg; metal ions $1 \times 10^{-2}M$, 10 ml.

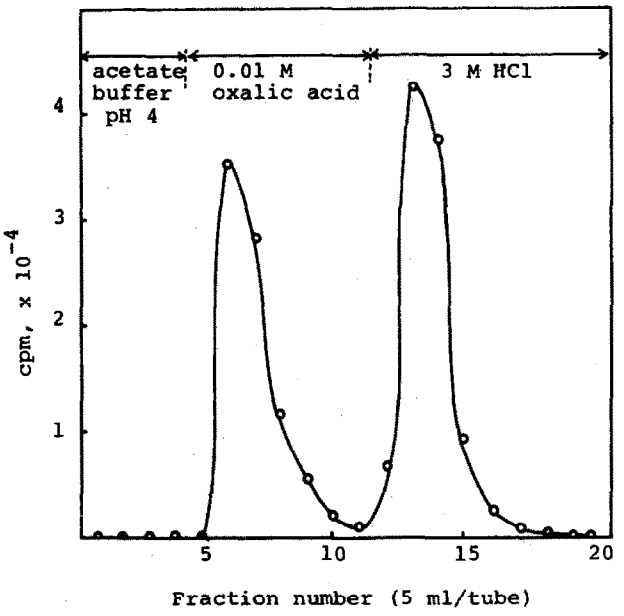


Fig. 3. Separation of iron(III) and cobalt(II) on resin III.

the time required for 50% uptake of cobalt(II) from the buffer solution was found to be 30 min. However, it was 60 min in the case of the hydrogen-form. The sodium-form was therefore used for column operation, to attain equilibrium quickly.

In Table 1, the effect of diverse substances on the sorption of cobalt(II) is shown. The presence of glycine does not interfere with sorption of cobalt(II). Ethylenediaminetetra-acetic acid, which forms a more stable chelate with cobalt(II), caused a significant decrease in the sorption of cobalt(II).

In a column study (0.5 × 11.5 cm, resin III 1 g), cobalt(II) could be retained from 50 ml of $1 \times 10^{-5}M$ solution (pH 4.0) almost quantitatively at a flow-rate of 2 ml/min. In addition, similar experiments were carried out in the presence of sodium chloride (0.1–3%). No leakage of cobalt(II) was observed under the experimental conditions. Hence it is expected that this resin can be applied to the concentration and separation of cobalt(II) from sea-water. A sea-water sample spiked with 1 ppm of cobalt(II) was passed through the column at a flow-rate of 1 ml/min. The leakage of cobalt(II) after passage of 120 and 320 bed-volumes of sample was 3.4 and 4.6%, respectively.

Table 1. Effect of chelating agents on sorption of cobalt(II) ($1 \times 10^{-4}M$, 10 ml)

Chelating agents	Cobalt(II) sorbed, % pH 3	pH 4
Glycine $1 \times 10^{-4}M$	89	100
$1 \times 10^{-3}M$	88	100
EDTA $1 \times 10^{-4}M$	47	46
$1 \times 10^{-3}M$	0	0
None	89	100

As an example of the application of resin III, iron(III) and cobalt(II) were separated. As shown in Fig. 3, iron(III) and cobalt(II), which are both retained on the column, could be almost quantitatively recovered by stepwise elution with oxalic acid solution and hydrochloric acid. However, in this procedure, only 50% of the cobalt(II) was recovered when the column was allowed to stand for 24 hr after sorption of the metal ions. This is accounted for by the oxidation of cobalt(II) to the tervalent species, which forms a more stable chelate with the functional groups on the resin.

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AMPEROMETRIC COMPLEX-FORMATION TITRATIONS WITH A DROPPING INDIUM AMALGAM ELECTRODE IN HALIDE MEDIUM

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Summary—The applicability of a dropping indium amalgam electrode for the determination of metal ions in the presence of large concentrations of halides by means of amperometric complex-formation titrations using normal pulse polarography has been investigated. Titrations appear to be possible in the presence of 4*M* potassium iodide, 1*M* potassium bromide and 1*M* potassium chloride.

In previous papers,[1,2] amperometric complex-formation titrations of metal ions with end-point indication by means of a dropping bismuth amalgam electrode and a dropping lead amalgam electrode have been discussed. With the bismuth amalgam electrode the interference from halides was considerably lower than that with the DME and rotating mercury electrode (RME). With the use of a lead amalgam electrode the interference from chloride and bromide ions was almost completely eliminated and even titrations in 0.01*M* iodide appeared to be possible. To complete this investigation other amalgams such as those of cadmium and indium would be worth considering with a view to making titrations possible in the presence of larger iodide concentrations. Indium was chosen because of the high value of the stability constant for the In(III)–EDTA complex and because of the low values of the stability constants for In(III)–halide complexes, particularly those with iodide. According to the literature[3] the values of log β_{1-4} are 2.70, 3.20, 4.20 and 3.30 for chloride, 2.10, 2.40, 2.50, and 0.60 for bromide and 1.35, 1.40, 1.30 and 0.50 for iodide. The value of log $K_{\text{In(III)EDTA}}$ is 24.95.[4]

EXPERIMENTAL

The amalgam for the dropping amalgam electrode was prepared by dissolving pure metallic indium (99.99%) in mercury in the same way as described earlier for the lead amalgam.[2] The concentration of indium in the amalgam was $1.6 \times 10^{-3}M$. The apparatus, including the titration cell used, was the same as in the case of the bismuth amalgam electrode[1] but the coulometer and platinum electrode were left out. The indium amalgam was prepared and stored under nitrogen. Even then, the concentration of the indium in the amalgam was found to be considerably lower after 3 days. This was caused by oxidation of indium from the amalgam by traces of oxygen. The oxidation was avoided by maintaining the amalgam at −0.85 V *vs.* SCE when not in use, by means of a voltage source (Knick S16) and an SCE placed in the supernatant solution (made 0.1*M* in potassium chloride) in the amalgam reservoir.

The amalgam at the narrow outlet at the bottom of the titration cell was maintained at −0.85 V *vs.* SCE in order to eliminate oxidation of the indium from the amalgam. For this purpose another SCE was placed in the titration vessel.

All experiments were performed with a PAR model 174 polarographic analyser in the normal pulse mode if not stated otherwise. All potentials were referred to the SCE.

Reagents and procedure were the same as given before.[1]

RESULTS AND DISCUSSION

From the literature[5–7] it is known that the reduction of In(III) to In and the reverse reaction are stepwise processes. If the rate-determining step becomes slow, for instance in solutions containing perchlorate, sulphate and hydroxide ions only, an irreversible electrode process is observed. However, in solutions containing halide ions the electrode process is reversible.

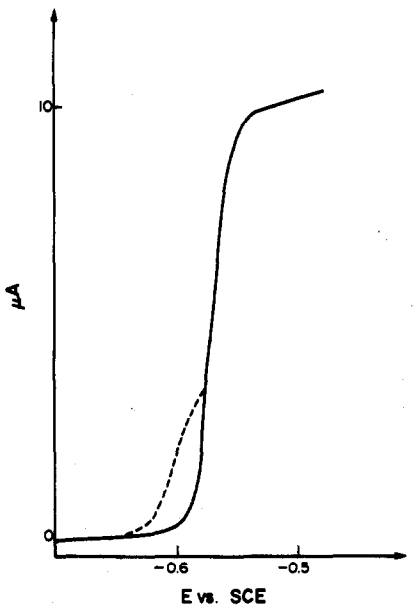

Fig. 1. Current-sampled d.c. polarogram of 1*M* KI at pH 4.8 in 0.02*M* acetate buffer in the presence (– – –) and absence (——) of about $2.5 \times 10^{-4}M$ EDTA.

Table 1. Titrations of metal ions with EDTA in the presence of halide ions

Indication potential *vs.* SCE, *V*	Conc. of the other ions	Species titrated, *μg/10 ml* Taken		Found	Error, %	Std. devn., % (no. of detns.)
−0.625	0.1*M* KI 0.02*M* acetate buffer pH 4.8	6.54	Zn(II)	7.07*	+8.1	7.6 (6)
−0.625	0.1*M* KI 0.02*M* acetate buffer pH 4.8	6.54	Zn(II)	6.52	−0.3	2.6 (4)
−0.625	1*M* KI 0.02*M* acetate buffer pH 4.8	6.54	Zn(II)	6.64	+1.5	4.0 (4)
−0.630	4*M* KI 0.02*M* acetate buffer pH 4.8	6.54	Zn(II)	6.59	+0.7	6.8 (5)
−0.600	1*M* KI 0.001*M* HCl pH 3.2	6.54	Zn(II)	6.57	+0.5	5.1 (4)
−0.640	1*M* KCl 0.02*M* acetate buffer pH 4.8	6.54	Zn(II)	6.92	+5.8	7.0 (4)
−0.630	1*M* KBr 0.02*M* acetate buffer pH 4.8	6.54	Zn(II)	6.97	+6.5	2.0 (5)
−0.625	1*M* KI 0.02*M* acetate buffer pH 4.8	6.70	VO^{2+}	6.54	−2.3	7.3 (6)
−0.625	1*M* KI 0.02*M* acetate buffer pH 4.8	0.654	Zn(II)	0.647	−1.1	8.4 (5)

* Without cathodic protection of the amalgam at the bottom of the titration cell.

The stepwise oxidation of indium implies that lower oxidation states than In(III), although disproportionating at high concentrations to In(III) and In, may exist at low concentration.[7] The disproportionation of indium(I) is catalysed by diluted indium amalgam. However, in the presence of iodide, insoluble brownish-red InI may be deposited at the electrode surface, particularly at solid electrodes ($K_{So}^{InI} = 2.2 \times 10^{-7}$).[7]

From an experiment with a dropping indium amalgam electrode at a potential in the region of the limiting current for the oxidation of In to In(III), in a 4*M* potassium iodide solution, no insoluble InI could be observed at the electrode surface. This suggested that no complications of this kind were to be expected during the investigation.

In order to investigate the applicability of the indium amalgam electrode as an end-point detector in amperometric complex-formation titrations, current-sampled d.c. polarograms obtained with a dropping indium amalgam electrode in acetate medium at pH 4.8 were recorded in the presence and absence of EDTA in solutions containing halide ions. Figure 1 shows such a polarogram in 1*M* iodide. A linear relationship was found between the height of the anodic ligand wave and the concentration of the ligand, as in the case of other amalgams investigated previously.[1,2]

The applicability of the indium amalgam electrode in halide medium is summarized in Table 1. From this table it can be seen that a systematic error is observed if the amalgam on the bottom of the titration cell is not maintained at a potential of −0.85 V *vs.* SCE. The concentration of the acetate buffer used was 0.02*M*. At higher concentrations, *e.g.*, about 0.1*M*, acetate interferes owing to the relatively large

Table 2. Maximum allowable values for halide ion concentrations at pH ~ 5 in anodic amperometric complex-formation titrations with EDTA

	Rotating mercury electrode	Dropping bismuth-amalgam electrode	Dropping lead-amalgam electrode	Dropping indium amalgam electrode
Cl^-	$10^{-3}M$	$5 \times 10^{-2}M$–0.1*M*	~4*M*	1*M*
Br^-	$10^{-5}M$	$10^{-2}M$	1*M*	1*M*
I^-	Impossible	Impossible	$10^{-2}M$	4*M*
Ref.	8	1	2	This work

value of the stability constant of the In(III)–acetate complex (log $\beta_3 = 10$).[4] Titrations at pH 3 can be performed in dilute hydrochloric acid solution.

The su given in the previous paper[2] for the interferences from halide ions at about pH 5 for anodic amperometric complex-formation titrations using a DME/RME and different dropping amalgam electrodes for the indication of the end-point can be extended as given in Table 2.

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DETERMINATION OF SULPHUR BY ELECTROLYTIC HYDROGENATION

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Summary—Certain sulphur compounds such as thiosulphuric acid, polythionic acids, thiocyanic acid, thioureas, thioamides and 2-mercapto-acids are readily electrolytically hydrogenated in 1*N* sulphuric acid to form hydrogen sulphide which is absorbed in potassium hydroxide solution and titrated with *o*-hydroxymercuribenzoic acid in the presence of dithizone as indicator. The electrolytic cell consists of a lead anode in 5*N* sulphuric acid, a porous ceramic tube as diaphragm, and a cathode made of soft iron. The first-order rate-constants of hydrogenation and the results of determination of sulphur in some sulphur compounds are presented. The limit of determination is 0.1 ppm.

The hydrogenation of sulphur in sulphur compounds to form hydrogen sulphide offers a very attractive analytical approach because hydrogen sulphide can be determined with a good accuracy and sensitivity. The observation that hydrogen sulphide is evolved in the course of electrolysis of certain sulphur compounds is reported in the literature, but without analytical application. The electrolytic hydrogenation of some thioamides to yield amines and hydrogen sulphide was investigated by Kindler.[1] Similar results have been obtained in hydrogenation of thiocaprolactam[2] and rhodanine.[3] Rambacher and Mäke[4] have discovered that 2-mercapto-acids are electrolytically hydrogenated to give sulphur-free acids and hydrogen sulphide.

The present investigation was stimulated by the need for the control of effluents and of pollution of natural water containing sulphur compounds. It seems that the approach based on electrolytical hydrogenation should be a very useful one, and may be adapted for automatic analysis.

EXPERIMETAL

Apparatus

The cell recommended for electrolytic hydrogenation of sulphur compounds is shown in Fig. 1. It is composed of two glass vessels, a lead anode, a porous ceramic tube (outer diameter 12 mm, inner diameter 9 mm, length 220 mm), and a strip (8 mm breadth) of soft iron as cathode. The iron strip tapers to 2 mm at the top and penetrates the rubber plug. The two glass vessels are tightly joined together by means of a plug formed of a silicone rubber tube with the ceramic tube inserted in its upper end, and the glass capillary tube in its lower end. The inlet and outlet of the outer vessel are used for circulating water from a thermostat. The anode compartment is filled with 5*N* sulphuric acid. The hydrogen and hydrogen sulphide evolved are directed from one of the outlets at the top of the cathode compartment (the other being closed) through a PVC tube (bore 1.5 mm) and a glass capillary tube into a conical absorption and titration vessel (top diameter 20 mm, bottom diameter 6 mm, height 100 mm).

Reagents

The preparation of *o*-hydroxymercuribenzoic acid (HMB) and titration of sulphide have already been described.[5] The concentrations of the test sulphur compounds were calculated either from the weights used or determined by a well established procedure.

Procedure

Adjust the temperature by means of a stream of water passing through the outer mantle from the thermostat. Fill the anode compartment with 5*N* sulphuric acid. Rinse the cathode compartment with 1*N* sulphuric acid and close the capillary tube at the bottom of the cathode compartment with a tight rubber cap. By means of a rubber tube, attach a small funnel to one outlet at the top of the cathode compartment, keeping the other one open, and through it transfer 10 ml of the neutral sample and 1 ml of 11*N*-sulphuric acid into the cathode compartment, close the open outlet with a rubber cap, remove the funnel and attach the PVC tube leading to the capillary tube dipping into 5 ml of 0.2*M* potassium hydroxide in the absorption vessel. The hydrogen sulphide absorbed can be directly titrated with HMB, with dithizone as indicator. Adjust the electrolysis current to 3.5 A and titrate the solution in the absorption vessel at 5-min intervals with 2×10^{-4}–0.05*N* HMB solution until the purple colour does not change back to yellow within 5 min. At 25° most determinations are completed in 20 min, and a few in 30 min. If this is not the case the hydrogenation should be repeated at a higher temperature.

Note. The procedure is not directly applicable to alkaline samples containing compounds which are rapidly decomposed in acid solution. Such compounds should be removed first, and an extraction with 0.01*M* tributyltin chloride in iso-octanol is recommended. The following pH-values are suitable for extraction of interfering compounds: sulphide 10–11, polysulphide 8–9, dithiocarbamates 7–9, xanthates 6–8. Sulphite, if any, can be oxidized to sulphate by adding the sample (10 ml) with stirring to 10 ml of a solution containing the previously determined quantity of iodine needed for oxidation of the sample in acid solution, and enough sulphuric acid to give the final sulphuric acid concentration of 1*N*. The oxidation of sulphur compounds other than sulphite with iodine in acidic solution does not influence the hydrogenation to hydrogen sulphide because the oxidation products are readily reducible.

RESULTS AND DISCUSSION

The rate of hydrogenation, expressed as the rate

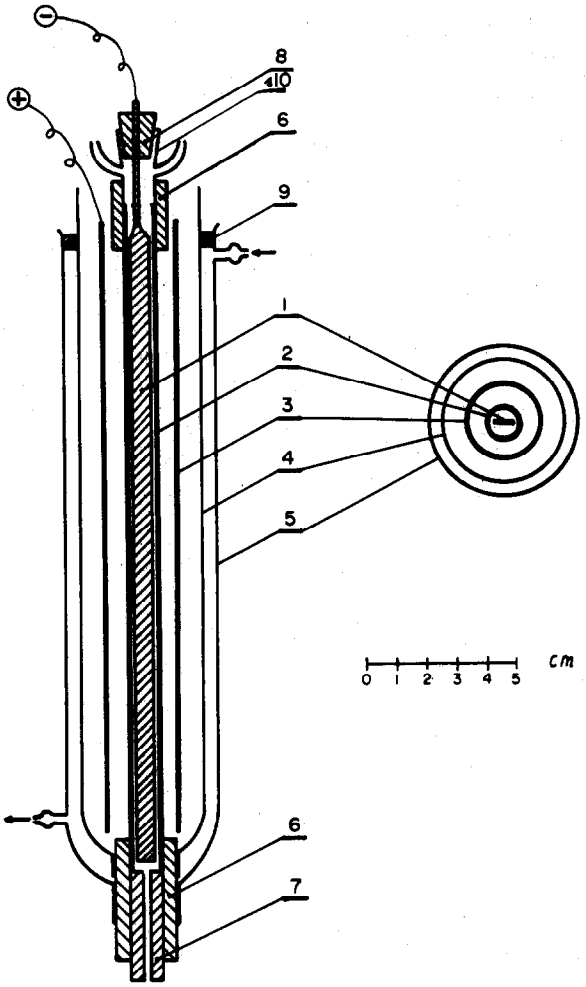

Fig. 1. Vertical and horizontal cross-sections of the electrolytic cell for hydrogenation of sulphur compounds. 1—Cathode, 2—ceramic tube, 3—lead anode, 4—inner glass vessel, 5—outer glass vessel (the thermostatic mantle), 6—silicone rubber tube, 7—glass capillary tube, 8—rubber plug, 9—tightening ring, 10—glass tube with outlets.

of evolution of hydrogen sulphide, approximates to a first-order relationship:

$$k = \frac{1}{t} \ln \frac{X_\infty}{X_\infty - X_t}$$

where X_∞ is the total hydrogen sulphide evolved, X_t is the hydrogen sulphide evolved after time t. The rate constants calculated from this formula are summarized in Table 1. Calculation of the rate constant may be of interest for characterization of an unknown sample. Many sulphur compounds cannot be electrolytically hydrogenated under the mild conditions suggested in this paper; they include sulphuric acid, sulphamic acid, aliphatic and aromatic sulphonic acids, sulphonamides, thioethers and thiols (with the exception of 2-mercapto-acids). Sulphur dioxide is about 50% converted into hydrogen sulphide, the rest being converted into elemental sulphur. The rate of hydrogenation increases with increasing concentration of sulphuric acid but only very slightly at sulphuric acid concentrations of about 1*N*.

Increase in temperature from 25° to 75° increases the rate constant by a factor of 6 for thiourea and 2-thiouracil, and 2.5 for ethylene thiourea.

The influence of the cathode material on the rate of hydrogenation is different for different compounds. As may be seen from Table 1 the rate of hydrogenation of thiosulphate is not seriously influenced by the cathode material. On the other hand, the rate of hydrogenation of thioglycollic acid and thioacetamide is drastically reduced when the iron cathode is replaced by a silver cathode. The hydrogenation of thiocyanic acid to form hydrogen sulphide depends strongly upon the cathode material. At an iron cathode the conversion is quantitative, but with silver or lead is only fractional, the rest being converted into an unidentified compound. A copper cathode is not suitable for analysis of sulphur compounds because

Table 1. Electrolytic hydrogenation of sulphur compounds to hydrogen sulphide: area of cathode—32 cm^2, current density at cathode 11 A/dm^2, volume of catholyte 11.5 ml, temperature 25°

Compound	Cathode	Sulphur		Recovery, %	Rate constant, min^{-1}
		Taken, *mg*	Found, *mg*		
Thiosulphate	Iron	1.28	1.25	97.6	0.37
Trithionate	Iron	0.765	0.756	98.8	0.22
Tetrathionate	Iron	1.28	1.27	99.2	0.31
Thiocyanate	Iron	1.28	1.28	100.0	0.18
Thioglycollic acid	Iron	1.39	1.38	99.3	0.17
Thiomalic acid	Iron	0.70	0.71	101.4	0.26
Rubeanic acid	Iron	1.35	1.36	100.7	0.24
Thioacetamide	Iron	1.10	1.09	99.1	0.25
Thiocaprolactam	Iron	1.20	1.20	100.0	0.22
6-Mercaptopurine	Iron	1.10	1.12	101.8	0.10
Thiourea	Iron	1.06	—	—	0.025
Thiourea*	Iron	1.06	1.07	100.9	0.15
Ethylene thiourea	Iron	1.45	—	—	0.053
Ethylene thiourea*	Iron	1.45	1.46	100.7	0.13
2-Thiouracil	Iron	1.49	—	—	0.040
2-Thiouracil*	Iron	1.49	1.49	100.0	0.24
Thiosulphate	Lead	1.28	1.26	98.4	0.35
Trithionate	Lead	1.28	1.27	99.2	0.27
Tetrathionate	Lead	1.28	1.27	99.2	0.36
Tetrathionate	Silver	1.28	1.27	99.2	0.32
Thioglycollic acid	Silver	1.39	—	—	0.067
Thioacetamide	Silver	1.10	—	—	0.080
Tetrathionate	Copper	1.28	1.24	96.8	0.30
Thiocyanate	Copper	1.28	1.22	95.4	0.20
Thioglycollic acid	Copper	1.39	1.20	86.3	0.31
Thioacetamide	Copper	1.10	0.98	89.1	0.20

* Temperature 75°.

part of the sulphur is retained on the surface as copper sulphide. So far, the iron cathode has proved best.

The results of determination of sulphur in a group of sulphur compounds are listed in Table 1. Most are satisfactory, the error being less than 1%. In order to increase the rate of hydrogenation some compounds were treated at 75°.

Table 2 presents the results of determination of reducible sulphur in trace quantities, as exemplified by sodium tetrathionate. In this case the hydrogen sulphide was titrated with 10^{-3} and $2 \times 10^{-4}N$ HMB. At the level of 25 μg of reducible sulphur in 10 ml of sample, the error is still only about 1%, and at the 5-μg level it amounts to about 5%. The practical lowest limit of estimation may be accepted as 1 μg in 10 ml, *i.e.*, 0.1 ppm of reducible sulphur.

Table 2. Determination of sulphur in sodium tetrathionate by electrolytic hydrogenation at 25° on iron cathode

Sulphur		Mean recovery, %
Taken, μg	Found, μg	
25.6	25.4, 25.6, 25.8, 25.4, 25.1	99.6
5.12	5.42, 5.53, 5.08, 5.31, 5.25	104

CONCLUSIONS

The analytical procedure based on the electrolytic hydrogenation of sulphur compounds to hydrogen sulphide may be recommended for use in the following fields.

1. Estimation of sulphur pollution in effluents and in natural water, involving thiosulphate, trithionate, tetrathionate, thiocyanate, thioureas, thioamides and 2-mercaptoacids. On the other hand sulphide, polysulphides, sulphite, xanthates, dithiocarbamates and sulphate must be determined separately.

2. Determination of reducible sulphur compounds in different preparations and in the presence of non-reducible sulphur compounds, *e.g.*, selective determination of thiomalic acid in the presence of cysteine, cysteamine, methionine, 3-mercaptopropionic acid, 2-mercaptoethanol and thioglucose.

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ANALYTICAL DATA

METAL CHELATES OF PHOSPHONATE-CONTAINING LIGANDS—II

STABILITY CONSTANTS OF SOME β-STYRYLPHOSPHONIC ACID METAL CHELATES

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Summary—The synthesis and properties of β-styrylphosphonic acid (SPA) are reported. The values of the protonation constants of the ligand were determined potentiometrically at different ionic strengths and in the temperature range 0–65°. The enthalpy and entropy of protonation have been calculated by using the van't Hoff isochore. The protonation process is endothermic and is stabilized by a relatively large positive entropy change. The stability constants of the complexes formed between SPA and the bivalent Mg, Ca, Ba, Co, Ni and Pd ions at 25° and ionic strength of 0.12*M* KNO_3 were also determined. All measurements were carried out in 18% dimethylformamide–water mixture.

Although the complexes of metal ions and phosphonate-containing ligands has been studied by several authors,[1–11] the work has been confined to certain types of organic phosphonate complexes.

The present paper describes the preparation and the properties of β-styrylphosphonic acid monomer. The values of the protonation and stability constants of the bivalent magnesium, calcium, barium, cobalt, nickel and palladium complexes were measured.

EXPERIMENTAL

Reagents and procedure

Pure recrystallized β-styrylphosphonic acid, monosodium salt, (C_6H_5–CH=CH–PO_3HNa), was prepared by adding a suspension of phosphorus pentachloride in dry benzene (0.2 mole) to a benzene solution of styrene (0.1 mole). The mixture was stirred and left overnight. The yellowish suspension of the PCl_5 addition-product of styrene (C_6H_5–CHCl–CH_2PCl_4.PCl_5) was then filtered off and hydrolysed with ice to give β-styrylphosphonic acid. The acid was purified by slowly adding a solution of it in dilute sodium hydroxide, with stirring, to warm dilute hydrochloric aicd. White needles of the monosodium salt (m.p. 230°) were isolated. The compound was then characterized by means of chemical analysis, and electronic and infrared spectroscopy (*vide infra*).

A stock solution of the ligand was prepared by dissolving the appropriate amount in 30% warm pure dimethylformamide. Metal nitrate solutions (except for palladium, for which the chloride salt was used) were prepared, standardized with EDTA and diluted as required. All reagents were of analytical grade.

The procedure involved a potentiometric titration of an acidified solution of β-styrylphosphonic acid monosodium salt ($6 \times 10^{-3}M$) with standard potassium hydroxide solution in the absence and presence of magnesium, calcium and barium ions at 1:3 and 1:6 molar ratios of metal to ligand. For nickel, cobalt and palladium the molar ratio was kept as high as 1:15 in order to prevent precipitation during the titration. The volume of the titration solution was 50 ml and the ionic strength was maintained at 0.12*M* with potassium nitrate.

The potentiometric measurements were made with a digital Radiometer pH M62 pH meter fitted with a combined glass–calomel electrode and kept thermostatically at the required temperature. The electronic spectrum of the ligand was obtained with a Unicam SP 800 spectrometer. The infrared spectrum was recorded (KBr disc) in the range 3800–625 cm^{-1} with a Unicam SP 1000 spectrometer.

RESULTS AND DISCUSSION

The strongest bands obtained in the infrared spectrum of the ligand at 738 and 695 cm^{-1} suggest the presence of a monosubstituted benzene ring. The prominent band at 985 cm^{-1} together with the bands at *ca.* 1635, 1620 and 1583 cm^{-1} are taken as evidence for the presence of a vinyl group attached to the ring. The intense *K*-band in the ultraviolet spectrum (*cf.* Table 1) at 269 nm ($\log \epsilon_{max} = 4.134$) argues for this conjugation. The next most intense bands in the infrared spectrum at 1452 and 1202 cm^{-1} are probably due to the presence of the P–C and hydrogen-bonded P=O groups respectively. The presence of the P–OH group is indicated by the shallow broad band at 2800–2700 cm^{-1}, which disappears upon chelation.[12–14]

The titration curve of the free ligand shows two inflections at $a = 2$ and $a = 1$, corresponding to the first and second protonation steps respectively.

Table 1. Spectral data for β-styrylphosphonic acid (monosodium salt)

λ_{max}, nm	log ϵ_{max}
269	4.134
280 (s)	3.435
292	3.192

(s) = shoulder.

Table 2. Protonation constants of β-styrylphosphonic acid at various ionic strengths in 18% DMF–water mixture (25°C)

I	log K_1	log K_2
0 (extrapolated)	8.36	3.60
0.08	7.74	3.31
0.12	7.61	3.23
0.20	7.38	3.14
0.30	7.41	3.18

Since the difference in the logarithms of the successive protonation constants is greater than 2.8,[15] equation (1) was used to calculate the values of K_i ($i = 1$ or 2).

$$\log K_i = \log \frac{(3 - a - i)C_{H_2SP} - [H^+] + [OH^-]}{(a - 2 + i)C_{H_2SP} + [H^+] - [OH^-]} + pH \quad (1)$$

where C_{H_2SP} is the total ligand concentration and a is the number of meq of base added per mole of ligand.

The values of the stability constants were determined graphically after the method of Rossotti and Rossotti.[16] The function,

$$F = \frac{\bar{n}}{(1 - \bar{n})[SP^{2-}]} = \beta_1 + \beta_2 \frac{(2 - \bar{n})}{(1 - \bar{n})}[SP^{2-}] \quad (2)$$

was used, where $[SP^{2-}]$ is the concentration of the free unprotonated styrylphosphonate ligand. Calculated values of $\bar{n}$ and $[SP^{2-}]$ were obtained from the titration graphs by using the functions

$$[SP^{2-}] = \frac{(2 - a)C_{H_2SP} - [H^+] + [OH^-]}{[H^+]K_1 + 2[H^+]^2K_1K_2} \quad (3)$$

$$\bar{n} = \frac{C_{H_2SP} - [SP^{2-}]\alpha_{H_2SP}}{C_M} \quad (4)$$

where

$$\alpha_{H_2SP} = 1 + K_1[H^+] + K_1K_2[H^+]^2 \quad (5)$$

and C_M is the total metal concentration.

For calculating the hydrogen-ion concentration from pH measurements, the activity coefficients, $f\pm$, were obtained by using the Davies equation.[15]

Table 2 summarizes the values of log K_i obtained, as a function of the ionic strength (I) at 25° in 18% dimethylformamide–water mixture. A plot of log K_i *vs.* $\sqrt{I}$ gives a straight line at low values of I (*cf.* Fig. 1). The deviation of the values of log K_i at $I = 0.3$ is probably due to the increase in the degree of association of the supporting electrolyte with the ligand. Extrapolation of the linear part to zero ionic strength gives the values of 8.36 and 3.6 for log K_1 and log K_2 respectively.

The values of the enthalpy of protonation, ΔH^0, were obtained from the protonation constants measured over the temperature range 0–65° (*cf.* Table 3) by means of the relationship

$$\Delta H^0 = \frac{2.303\, RT_1T_2 \log(K_{T_2}/K_{T_1})}{(T_2 - T_1)}. \quad (6)$$

The free-energy change, ΔG^0, and entropy change, ΔS^0, were calculated for the two protonation reactions

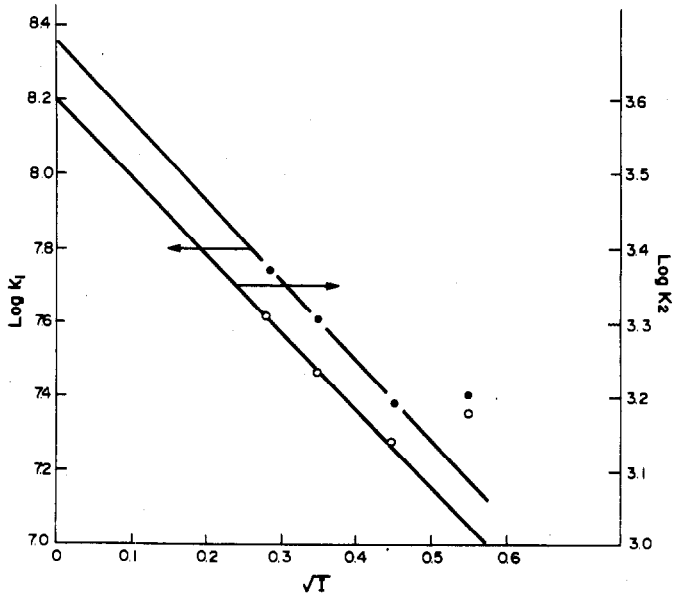

Fig. 1. A plot of log K_1 (log K_2) *vs.* the square root of the ionic strength.

Table 3. Protonation constants of β-styrylphosphonic acid determined at different temperatures (I = 0.2M KNO_3 in 18% DMF–water mixture)

Temperature, °C	log K_1	log K_2
0	7.25	3.08
25	7.38	3.14
37	7.43	3.21
65	7.58	3.35

Table 4. Thermodynamic parameters for the protonation of β-styrylphosphonic acid (I = 0.2M KNO_3 in 18% DMF–water mixture)

Protonation step	$\Delta H°$, *kcal/mole*	$\Delta G°_{25}$ *kcal/mole*	$\Delta S°$, $cal.mole^{-1}.deg^{-1}$
First	2.09	−10.03	40.7
Second	1.88	−4.27	20.6

involved, by using equations (7) and (8).

$$\Delta G^0 = -RT \ln K \tag{7}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{8}$$

where R is the gas constant and T is the absolute temperature.

The values are given in Table 4. The results suggest that the driving force for protonation is the positive entropy change and that the reaction is opposed by the positive enthalpy change.

Evidence obtained from the titration curves shows that the stability sequence is in the order Mg < Ca < Ba < Co < Ni ≃ Pd and complex formation takes place only at a = 1 except for Ni and Pd. This excludes the possibility of having protonated complex species present in appreciable amounts in solution. All the curves are characterized by two sharp inflections at a = 1 and a = 2. The equilibrium constants calculated for the systems studied are given in Table 5. In all cases, except for Pd(II), the values of $\bar{n}$ did not exceed unity.

For the alkaline earth metals, the values of log β_1 increase with increasing radius of the metal ion. The values obtained are, in general, higher than those reported for many monodentate organic acids.[17]

Table 5. Formation constants of β-styrylphosphonic acid with bivalent ions at 25°C in 18% DMF–water mixture (I = 0.12M KNO_3)

	log β_1	log β_2
Mg^{2+}	1.96	—
Ca^{2+}	2.05	—
Ba^{2+}	2.50	—
Co^{2+}	2.56	—
Ni^{2+}	3.67	—
Pd^{2+}	3.33	6.55

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FORMATION CONSTANTS OF TERNARY COMPLEXES OF VANADIUM(IV) WITH PICOLINIC ACID AND SALICYLIC OR 5-SULPHOSALICYLIC ACID

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Summary—The formation constants, β_{MAL}, for the reaction $VO^{2+} + A^- + L^{2-} \rightleftharpoons VOAL^-$ [where HA = picolinic acid and H_2L = salicylic or 5-sulphosalicylic acid] have been determined at $30 \pm 1°$ ($\mu = 0.1$, KNO_3). Potentiometric evidence is presented for the simultaneous addition of both ligands to the metal ion to form the 1:1:1 ternary complex.

Studies have been made[1–3] of a number of systems where a ternary complex is formed in two steps which partly overlap, the pH-ranges for formation of the individual 1:1 complexes being different. They are now extended to ternary systems where both ligands form 1:1 complexes with the metal ion almost in the same pH range and ternary complex formation occurs in a single step.

EXPERIMENTAL

Standard solution of vanadyl sulphate was prepared as described earlier.[4] Solutions of pure picolinic (PA), salicylic (SA) and 5-sulphosalicylic (SSA) acids were prepared by direct weighing and standardized potentiometrically with potassium hydroxide. The pH-titrations were carried out at $30 \pm 0.5°C$ with a Cambridge pH-meter standardized with 0.05*M* potassium hydrogen phthalate. The ionic strength of the reaction mixture was kept approximately constant at 0.1 with potassium nitrate.

RESULTS AND DISCUSSION

The calculations of the dissociation constants of the ligands (PA, SA and SSA), and the equilibrium, chelate formation and hydrolysis constants for the 1:1 VO^{2+}–PA (SA or SSA) complexes and the corresponding mixed-ligand hydroxo complexes were described earlier.[1,5]

The potentiometric titration curves for PA, SA and SSA exhibited a sharp inflection at $m = 1$ (m = moles of base added per mole of metal ion or ligand), indicating the neutralization of the proton of the carboxylic group at low pH.

As reported earlier,[1,5] the potentiometric titration curves of vanadyl sulphate in the presence of an equimolar concentration of picolinic acid, SA or SSA may be explained on the basis of the formation of the 1:1 chelate and its further conversion into the corresponding monohydroxo complex.

When equimolar mixtures of vanadyl sulphate, PA and SA or SSA are titrated, only well-defined inflection is observed, at $m = 3$, attributable to the neutralization of the proton of picolinic acid and both protons of SA or SSA, the second being liberated as a result of chelation. These titration curves are at lower pH than those for the 1:1 systems from the very beginning, indicating the formation of a new species which can only be a 1:1:1 ternary complex. Further, it also indicates the simultaneous addition of both ligands to the metal ion. This is confirmed by the analysis of the potentiometric data, given below.

The equilibria involved in the mixed-ligand chelate formation, on the assumption that $VOAL_2^{3-}$, VOA_2L^{2-} *etc.* (HA = picolinic acid, H_2L = SA or SSA) are absent when the ratio of the reactants is 1:1:1, may be represented by:

$$VO^{2+} + HA + H_2L \rightleftharpoons VOAL^- + 3H^+$$

The equilibrium constant (K) of this reaction and the formation constant (β_{MAL}) of the 1:1:1 mixed-ligand chelate may then be given by the relations:

$$K = \frac{[VOAL^-][H^+]^3}{[VO^{2+}]([HA][H_2L]} \quad (1)$$

and

$$\beta_{MAL} = \frac{[VOAL^-]}{[VO^{2+}][A^-][L^{2-}]} = \frac{K}{k_1 k_1' k_2'} \quad (2)$$

where k_1 is the dissociation constant of picolinic acid and k_1' and k_2' are the first and second dissociation constants respectively of SA or SSA.

If T_M, T_A and T_L represent the total concentrations of the metal, primary ligand (HA) and secondary ligand (H_2L) species respectively and T_{OH} is the concentration of base added to the reaction mixture during the titration, then assuming that only mono-

Table 1. Dissociation constants of ligands and equilibrium and hydrolysis constants of 1:1 chelates [30 ± 1°C, μ = 0.1 (KNO_3)]

Ligand	pk_1	pk_2	pK_1	pK_H	$\log\beta_{MA_2}$
PA	5.28*	—	1.35*	3.32*	11.17*
SA	2.99†	13.60†	3.41†	8.04†	—
SSA	2.68†	11.42†	2.73†	7.07†	—

* Data from ref. 5.
† Data from ref. 1.

nuclear metal chelate species are formed, it follows that:

$$T_M = [VO^{2+}] + [VOA^+] + [VO(OH)A] + [VOL] + [VO(OH)L^-] + [VOAL^-] \quad (3)$$

$$T_{OH} + [H^+] = [VOA^+] + 2[VO(OH)A] + 2[VOL] + 3[VO(OH)L^-] + 3[VOAL^-] + [A^-] + [HL^-] \quad (4)$$

$$T_A = [VOA^+] + [VO(OH)A] + [VOAL^-] + [HA] + [A^-] \quad (5)$$

$$T_L = [VOL] + [VO(OH)L^-] + [VOAL^-] + [H_2L] + [HL^-] \quad (6)$$

The concentrations of OH^-, L^{2-} and hydrolysed species of the free vanadyl ions can be neglected, in the pH range studied, compared to those of other species present. For a 1:1:1 reaction mixture, by using equations (3)–(6) and the relations for the dissociation constants of the ligands and the equilibrium constants K_1, K_H, K'_1 and K'_H of the reactions

$$VO^{2+} + HA \rightleftharpoons VOA^+ + H^+;$$
$$VO^{2+} + HA + H_2O \rightleftharpoons VO(OH)A + 2H^+;$$
$$VO^{2+} + H_2L \rightleftharpoons VOL + 2H^+ \text{ and}$$
$$VO^{2+} + H_2L + H_2O \rightleftharpoons VO(OH)L^- + 3H^+$$

respectively, it may be shown that:

$$-a[VO^{2+}]^3 + b[VO^{2+}]^2 + c[VO^{2+}] - d = 0 \quad (7)$$

where

$$a = \frac{K_H C_L}{[H^+]^2} + \frac{K'_H C_A}{[H^+]^3}$$

$$b = C_A + C_L + \{(3-m)T_M - [H^+]\}C_A C_L + \frac{K_1 y}{[H^+]} - \frac{K'_H x}{[H^+]^3}$$

$$c = x + y + xy$$

$$d = \{(3-m)T_M - [H^+]\}xy$$

Table 2. Equilibrium and formation constants of mixed-ligand complexes [30 ± 1°C, μ = 0.1 (KNO_3)]

System	$-\log K$	$\log\beta_{MAL}$
VO^{2+}–PA–SA	3.24 ± 0.07	18.63 ± 0.07
VO^{2+}–PA–SSA	2.94 ± 0.17	16.44 ± 0.17

$$C_A = \left(\frac{K_1}{[H^+]} + \frac{K_H}{[H^+]^2}\right)$$

$$C_L = \left(\frac{K'_1}{[H^+]^2} + \frac{K'_H}{[H^+]^3}\right)$$

$$x = \left(1 + \frac{k_1}{[H^+]}\right)$$

$$y = \left(1 + \frac{k'_1}{[H^+]}\right).$$

The equilibrium concentration of free vanadyl ions present in the reaction mixtures at various points of the titration curves for the ternary systems was obtained by solving equation (7), with the help of the Newton–Raphson method.[6] By substitution of the values of K_1, K_H, K'_1 and K'_H given in Table 1, the concentrations of the other species involved in the equilibrium relations were then calculated from the equations above, and so were the values of the equilibrium constant K and the formation constants β_{MAL}. The values are presented in Table 2.

Comparison of the data in Table 2 reveals that the order of the overall stability constants of ternary complexes is the same as that of the 1:1 VO^{2+}–hydroxy-acid complexes and can be explained as earlier.[1] It is interesting to note that though the hydroxy-acids (SA and SSA) form a 1:1:1 mixed-ligand chelate in presence of picolinic acid, they have no tendency to form 1:2 simple complexes with vanadium-(IV). The formation of the mixed complex is due to the coloumbic attraction between the VOA^+ and the negatively charged carboxylate group present in the hydroxy-acids.

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ANNOTATION

BUFFERS FOR FLUORIDE ELECTRODE CALIBRATION IN THE LOW CONCENTRATION RANGE

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Summary—Thorium-buffered fluoride standards for calibration of fluoride electrodes at low fluoride concentration are described. Fluoride electrodes give Nernstian response down to very low fluoride levels, but the practical limit is set at about pF 6 by contamination from distilled water, reagents *etc.*

The detection limit for the lanthanum fluoride ion-selective electrode is often quoted as $10^{-6}M$ fluoride. However, it has been pointed out[1,2] that this is not the intrinsic detection limit due to solubility of the membrane material or adsorption at the membrane surface, but is a limit set by contamination in the distilled water or reagents used. Baumann[3] has shown that this electrode continues to give a Nernstian response down to very low levels of free fluoride (10^{-7}–$10^{-9}M$) in the presence of cations strongly complexed by fluoride. It therefore seemed of interest to develop a suitable range of metal-buffered fluoride standards.

EXPERIMENTAL

Measurements were performed with a home-made fluoride electrode employing an LaF_3 crystal doped with 0.05% of europium, and a reference calomel electrode Radiometer model K 401. A Metrohm EA 109 glass electrode was used for pH control. A Digital Ionalyzer model 801 A interfaced with an Orion digital printer model 751 was used.

All chemicals used were of analytical grade and the water was triply distilled from quartz apparatus.

Preparation of fluoride buffer solutions

To 10 ml of $0.01M$ thorium nitrate, 7.00 g of sodium perchlorate monohydrate and an appropriate volume of 0.01 or $0.001M$ sodium fluoride solution were added. The mixture was diluted to the mark, transferred to a polypropylene beaker and adjusted to pH 2.00 ± 0.05 with perchloric acid. This uncertainty in the pH causes an error of less than 0.01 in pF. Adjusting the pH in this way causes only a negligible increase (0.2–0.3%) in the volume.

Calculation of pF

To check the extent of Nernstian response of the electrode at low concentrations of fluoride, the composition of $10^{-3}M$ thorium(IV) solutions containing fluoride that would give free fluoride concentrations within the pF range 7.5–10.0 was calculated (Table 1) by means of the program HALTAFALL, translated from the original ALGOL version[4] into FORTRAN, with the equilibrium constants for the three-component system F^-, Th(IV), H^+ selected earlier by Anfält *et al.*[5]

Computer calculations were performed in the Institute of Mathematical Machines, Warsaw University, with the CDC Cyber system.

RESULTS

The results for electrode calibration with the buffered fluoride solutions are given in Fig. 1. Because these buffered solutions were prepared in $0.5M$ sodium perchlorate, the same medium was used for electrode calibration by dilution of standard fluoride solutions. The potentials were recorded after at least 30 min, when they were changing by less than 1 mV in a 10-min interval (Table 2). Taking into account the potential measured for $0.5M$ sodium perchlorate without addition of fluoride, the level at which trace contamination will have an effect can be estimated as $5 \times 10^{-7}M$. It causes the calibration curve to deviate from linearity at pF > 6. In the thorium-buffered fluoride solutions steady potential values were obtained after 20–60 min. All measurements were made on solutions stirred at constant speed, the potential being recorded at 1-min intervals. For both sets of calibrations the solutions were used in order of increasing fluoride-ion concentration.

Table 1. The total fluoride concentration in the solutions used for electrode calibration. Each solution $0.5M$ in $NaClO_4$, $0.001M$ in $Th(NO_3)_4$ and adjusted to pH 2.00 ± 0.05 with $HClO_4$

pF	Total fluoride concentration, M
10.0	4.0×10^{-6}
9.5	1.3×10^{-5}
9.0	4.0×10^{-5}
8.5	1.18×10^{-4}
8.0	3.06×10^{-4}
7.5	6.30×10^{-4}

Table 2. Changes of fluoride electrode potentials in fluoride buffer solutions

pF	Potentials, *mV* vs. *SCE*						
	10 min	20 min	30 min	40 min	50 min	60 min	70 min
10.0	455.6	473.1	483.3	486.0	487.6	489.1	489.9
9.5	482.5	485.8	488.0	488.8			
9.0	490.5	491.5	492.0				
8.5	472.1	468.6	464.9	462.2	460.4	459.6	
8.0	436.5	435.4	434.1	433.1			
7.5	400.9	399.6	398.9				

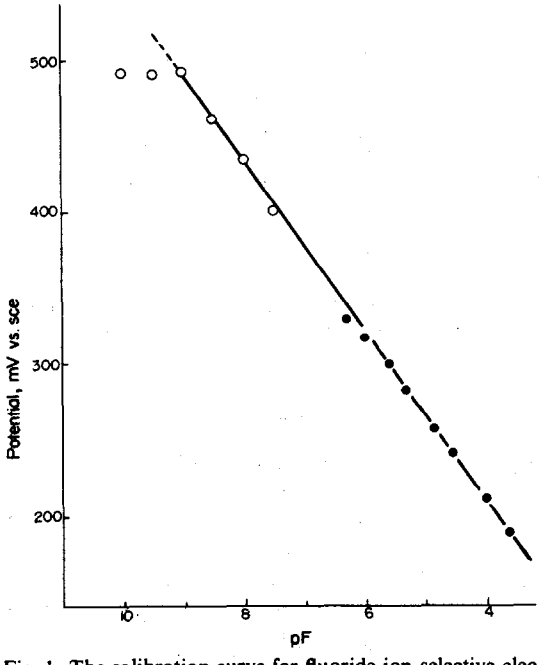

Fig. 1. The calibration curve for fluoride ion-selective electrode in 0.5*M* $NaClO_4$: ● calibration in diluted fluoride standard solutions, ○ calibration in fluoride ion buffered solutions.

The results obtained clearly indicate that the electrode gives Nernstian response to fluoride down to $10^{-9}M$. The procedure is analogous to the determination of the sensitivity of cationic membrane electrodes by use of the cation-buffered solutions introduced by Blum and Fog.[6] The results also suggest that the fluoride contamination in distilled water or chemicals, usually below the $10^{-6}M$ level, will cause errors only if pF is 10 or more.

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POLAROGRAPHIC DETERMINATION OF INDIUM(III) AFTER SALTING-OUT EXTRACTION OF THE BROMIDE COMPLEX INTO ACETONITRILE

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Summary—A simple and sensitive method has been developed for the polarographic determination of indium(III) after solvent extraction into acetonitrile, salted-out from aqueous solution with sodium bromide. The extracted indium(III)–bromide complex gives a well-defined d.c. wave with $E_{1/2} = -0.69$ V *vs.* SCE. The wave-height is directly proportional to the concentration of indium(III) from 1.6×10^{-6} to $3.0 \times 10^{-4}M$ with respect to the original aqueous solution. In the a.c. polarographic method, a linear calibration curve is obtained for indium(III) over the concentration range from 1.6×10^{-6} to $1.5 \times 10^{-5}M$, and interference from most foreign ions can be eliminated. In particular, 10.0 mg of Fe(III) and 2.5 mg of Tl(III) are tolerated when 1.0 g of ascorbic acid is added. The lower limit of determination is $8 \times 10^{-8}M$ indium(III) by the square-wave polarographic method.

Indium(III) in aqueous solution can be determined polarographically with good sensitivity, as it undergoes a reversible three-electron reduction at a dropping mercury electrode.[1] Interference from Cd(II), Tl(III) and Pb(II) is avoided by adding a suitable complexing agent such as potassium iodide[2] or potassium chloride.[3] A solvent-extraction procedure has been used for the removal of major constituents such as Tl(III) and Fe(III), before polarographic determination of indium(III).[4] Several studies have been reported on the direct polarographic determination of indium(III) after solvent extraction with oxine,[5] DDTC[6] or acetylacetone.[7] Although these extraction–polarographic methods are sensitive and selective, they are troublesome to use because the extract has to be mixed with other solvents for the polarographic measurement. It was the aim of the present study to develop a simple and selective procedure for the extraction–polarographic determination of indium(III).

In a previous investigation,[8] acetonitrile (AN) was exploited as the solvent for an extraction–polarographic determination of cadmium(II) based on the fact that the solvent can be separated from its aqueous solution by salting-out with ammonium sulphate. In the present study, this polarographic method of analysis has been applied to the direct determination of indium(III) in the AN extract, in which the ion is isolated and concentrated from aqueous solution. Sodium bromide is used as both the salting-out agent for the phase separation and the complexing ligand for the indium, and tetrabutylammonium bromide (TBAB) as both the counter-ion in the extracted ion-pair and the supporting electrolyte in the polarographic measurement. The proposed method is simple, selective and sensitive.

EXPERIMENTAL

Apparatus

A Yanagimoto polarograph, Model PA-202, was used or square-wave (sw) polarography. Other instruments used were the same as described previously.[8] The DME had the following characteristics: $m = 0.783$ mg/sec, $t = 4.70$ sec in AN at a mercury head of 60.0 cm.

Reagents

Standard indium(III) solution. Indium sulphate (0.339 g) was dissolved in 1 litre of water containing a small amount of sulphuric acid, to give an approximately $10^{-3}M$ solution which was then standardized by complexometric titration.

Sodium bromide (Wako Junyaku Chemicals) and TBAB (Tokyo Kasei Chemicals) were used without further purification. AN was purified by distillation once from phosphorus pentoxide to remove reducible impurities.[9] Other reagents were of guaranteed reagent grade.

Procedure

To 25.0 ml of acidic aqueous solution containing indium(III), 20.0 ml of $0.05M$ TBAB solution in AN were added, followed by 15.0 g of sodium bromide as the salting-out agent. The mixture was shaken for 1 min, then allowed to stand for 1 min. A portion of the extract was transferred into a polarographic cell, deaerated with nitrogen gas for 3 min, and the polarogram was recorded (*vs.* S.C.E.) at $25 \pm 0.1°$.

RESULTS AND DISCUSSION

Ternary phase diagram

Acetonitrile is separated from aqueous solutions by salting-out with sodium bromide. In this investigation the volumes of the resulting phases were measured when different amounts of sodium bromide were added to water–AN mixtures. The results are shown in Fig. 1. The ternary diagram obtained is expressed in terms of percentage by weight and represents the

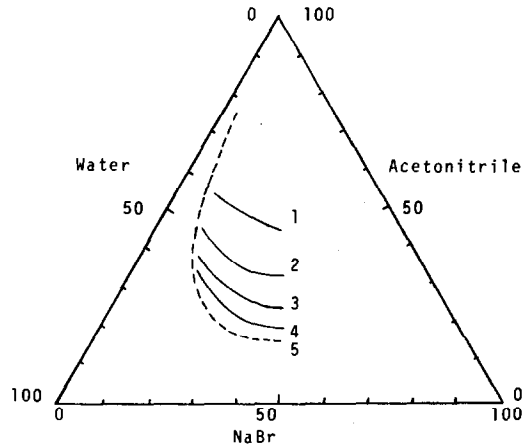

Fig. 1. Phase diagram of acetonitrile/water/sodium bromide 1, $V_w/V_0 = 1$; 2, $V_w/V_0 = 2$; 3, $V_w/V_0 = 5$; 4, $V_w/V_0 = 10$; 5 represents the compositions producing a homogeneous solution on dilution with water.

composition of water, AN and sodium bromide mixtures. The dotted line indicates the compositions from which a homogeneous solution is produced on addition of an excess of water, while the solid lines represent the compositions for which the volume-ratios of the two phases (V_w/V_0) are 1, 2, 5 and 10 after phase separation. The volume-ratio was 3.9 under the conditions of the procedure described.

Polarograms

Figure 2 illustrates the d.c. and a.c. polarograms of several metal bromides observed under the conditions described. The available potential range is from -0.36 to -1.45 V *vs.* SCE. The extracted In(III) complex gave a well-defined d.c. wave with $E_{1/2} = -0.69$ V and a sharp a.c. peak at the same potential. The d.c. wave of In(III) was diffusion controlled, and represented a three-electron reaction. The polarographic determination of the In(III) is considered to be reasonably selective since the $E_{1/2}$ is

Table 1. Effect of tetrabutylammonium bromide (TBAB) concentration on the d.c. wave- and a.c. peak-heights for $10^{-5}M$ In(III)

TBAB, *M*	i_d, μA	i_p	Volume of AN recovered, *ml*	$E_{1/2}$, *V*
0.005	—	218	10.0	—
0.010	0.276	222	10.0	−0.68
0.025	0.252	215	10.1	−0.69
0.040	0.255	210	10.2	−0.69
0.050	0.248	204	10.3	−0.69
0.060	0.240	196	10.5	−0.70
0.075	0.240	190	10.8	−0.71
0.100	0.211	169	11.0	−0.73

0.15 V or more apart from those of the other metal complexes. The Tl(III) complex gave two d.c. waves with $E_{1/2} = -0.35$ and -0.54 V. The second wave, which corresponds to Tl(I) → Tl(0) exhibited a maximum, and the a.c. peak was distorted. The Pb(II) complex gave a d.c. wave with maxima and a fair a.c. peak at -0.45 V. An ill-defined d.c. wave and no a.c. peak were observed in the case of the Cd(II) complex.

Effect of TBAB concentration

Table 1 shows the effect of increasing TBAB concentration on the d.c. and a.c. polarographic waves for an initial concentration of $10^{-5}M$ In(III). It was noted that the d.c. polarogram became well-defined at TBAB concentration above $0.01M$. As the concentration of TBAB is increased, the d.c. wave-height (i_d) and a.c. peak-height (i_p) decrease and the half-wave potential shifts towards more negative potentials. The decrease in the heights is probably ascribable to increase in the final volume and the viscosity of the AN phase and a salting-in effect due to TBAB. The shift of the $E_{1/2}$ is mainly correlated with the increase in the TBAB concentration of the AN phase, where

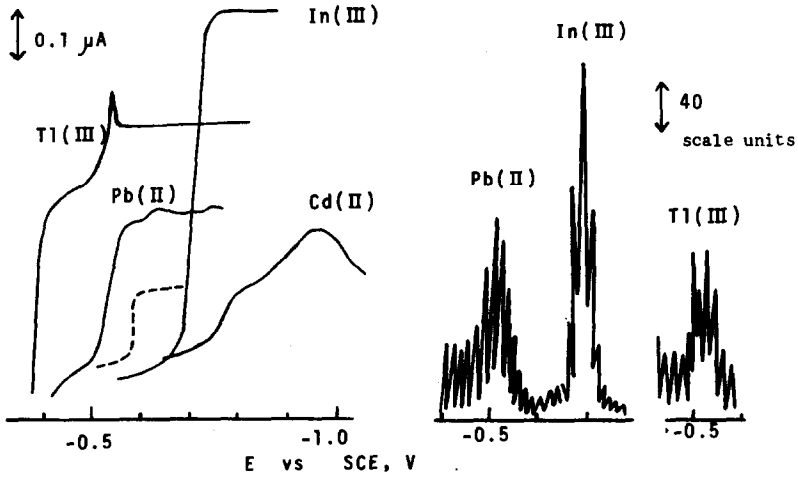

Fig. 2. Polarograms (d.c. and a.c.) of various metal bromides after extraction into acetonitrile. [Tl(III)] $2.55 \times 10^{-5}M$, [Pb(II)] $2.41 \times 10^{-5}M$, [In(III)] $1.44 \times 10^{-5}M$, [Cd(II)] $4.46 \times 10^{-5}M$. The broken line is the d.c. polarogram of $1.44 \times 10^{-5}M$ In(III) in $1.0M$ NaBr.

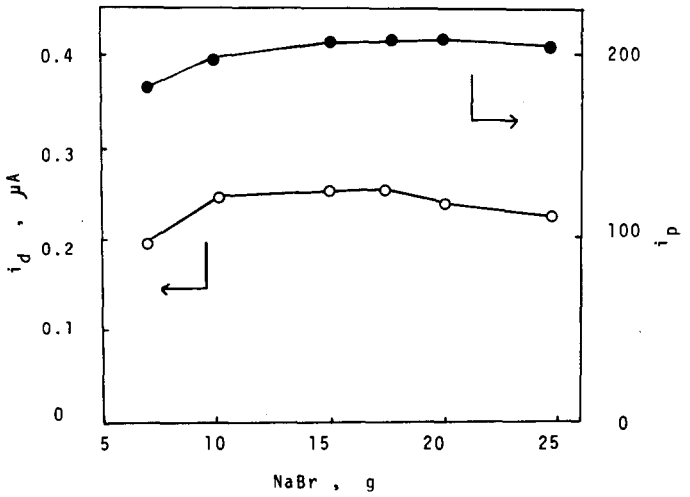

Fig. 3. Effect of sodium bromide concentration on d.c. wave-height and a.c. peak-height for $10^{-5}M$ In(III).

TBAB acts as both the counter-ion in the complex extracted and the supporting electrolyte. The 10.0 ml of extract obtained by following the recommended procedure had an electrolytic conductivity of 1.73×10^{-2} ohm^{-1}.cm^{-1}, a water content of 14.7‰, a viscosity of 0.463 cP, and a sodium bromide content of 68.0 mg (0.066*M*). A concentration of 0.05*M* TBAB in AN was chosen as being most suitable for the reagent.

Effect of sodium bromide concentration

The amount of sodium bromide taken was varied between 7.0 and 25.0 g. The results are shown in Fig. 3, from which it can be seen that i_d and i_p were approximately constant for the addition of amounts between 10 and 20 g. The volume of AN phase recovered increased with increasing amounts of sodium bromide up to 10 g, and became constant for amounts between 10 and 25 g. The half-wave potential shifted towards more negative potentials with increasing amounts of the salt, probably because of increase in the sodium bromide concentration in the AN phase, since the TBAB concentration in the AN phase remained constant. Hence 15 g was the amount of sodium bromide chosen for use in the standard procedure.

Effect of volume of aqueous phase

Values of i_d and i_p were obtained for extractions from different volumes of the original aqueous phase from 15 to 35 ml, as shown in Fig. 4. The heights increased greatly with increasing volume of the aqueous phase, because of the high degree of extraction and the decrease in volume of the AN phase. The volume of original aqueous phase taken must therefore be kept constant (25.0 ml).

Effect of pH

Extractions were carried out at different pH-values, adjusted by addition of 1.0*M* sulphuric acid or 1.0*M* sodium hydroxide. Figure 5 shows the plots of i_d and

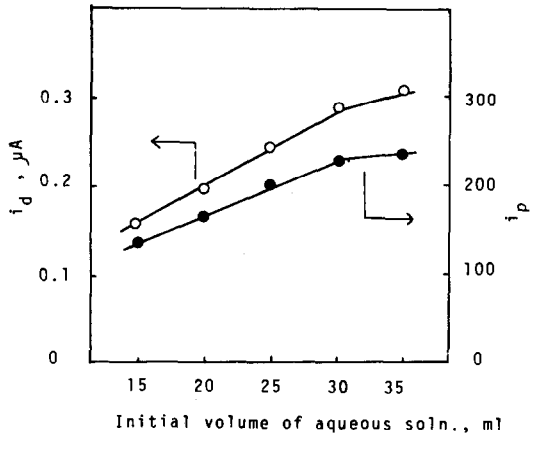

Fig. 4. Effect of initial volume of aqueous phase on d.c. wave-height and a.c. peak-height for $10^{-5}M$ In(III).

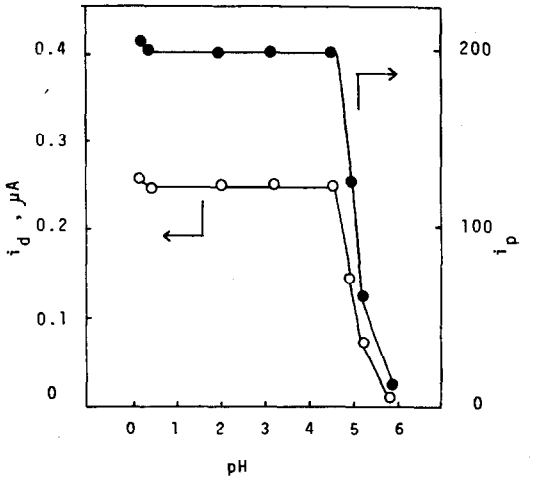

Fig. 5. Effect of pH on d.c. wave-height and a.c. peak-height for $10^{-5}M$ In(III).

Table 2. Effect of diverse ions on the determination of 27.7 μg of indium(III)

Species added	Amount of indium(III) added, mg	found, μg	Error,† %
Cu(II)*	0.5	27.9	+0.9
Fe(III)*	0.5	27.1	−2.1
Fe + ascorbic acid, 1 g	10.0	29.7	+0.9
Pb(II)*	2.5	28.0	+1.4
Cd(II)	10.0	27.4	−0.9
Tl(III)*	0.5	28.5	+3.1
Tl + ascorbic acid, 1 g	2.5	28.6	+3.3
Hg(II)*	0.5	26.8	−3.2
Bi(III)*	0.5	28.2	+1.9
Ca(II)	116.0	28.7	+3.8
Al(III)	100.0	27.5	−0.7
Ni(II)	100.0	27.8	+0.2
Zn(II)	100.0	28.0	+1.3
Co(II)	100.0	26.8	−3.2
Ag(I)	1.0	26.2	−5.3
F^-	12.9	26.5	−4.3
PO_4^{3-}	13.2	27.1	−2.0
SCN^-	11.4	27.9	+0.9
ClO_4^-	12.9	27.3	−1.4
CH_3COO^-	116.0	26.1	−5.8
VO_3^-	10.2	27.5	−0.5
MoO_4^{2-}*	1.0	27.4	−0.8
WO_4^{2-}	1.0	25.5	−8.0
$S_2O_4^{2-}$*	1.0	27.3	−1.4

* Denotes maximum amount tolerable within an error of ±4%.

† Based on mean of three determinations.

i_p against pH of the aqueous phase after extraction. It was found that the heights were approximately constant over the pH range 0.4–4.6. Over this pH range, the volume of AN phase recovered was constant (10.3 ml) and 99.5% of the In(III) complex was extracted in a single extraction.

Calibration curves

On the basis of these results, the procedure for the polarographic determination of In(III) was established. The d.c. and a.c. polarograms were recorded at various concentrations of In(III), while other conditions were kept constant. The calibration curves obtained were linear over the concentration ranges 1.6×10^{-6}–$3.0 \times 10^{-4}M$ In(III) for d.c. and 1.6×10^{-6}–$1.5 \times 10^{-5}M$ for a.c. polarography. The diffusion current constant of In(III) in the AN extract was 9.50 $\mu A.l.mmole^{-1}.mg^{-2/3}.sec^{1/2}$, about 4 times that obtained in $1M$ aqueous sodium bromide, as shown in Fig. 2. The relative standard deviation was 2.1% for 27.7 μg of indium(III) (10 determinations by a.c. polarography).

Effect of diverse ions

Possible interferences were investigated by a.c. polarography, which gave considerably better resolution for substances reduced at potentials close to each other. The results are summarized in Table 2. Cu(II), Fe(III), Pb(II), Cd(II), Tl(III), Hg(II) and Bi(III) were found to be tolerable at the levels tested. The interference caused by 10.0 mg of Fe(III) and 2.5 mg of Tl(III) could be eliminated by the addition of 1.0 g of ascorbic acid before the extraction step. Other cations such as Al(III), Ni(II), Zn(II) and Mn(II) showed no effect on the determination. Among the anions tested, MnO_4^-, CrO_4^{2-} and EDTA interfere seriously even in small amounts and must be excluded. Thiosulphate and tungstate were tolerable at levels up to 1 mg.

Square-wave polarography

Since the extract had a high electrical conductivity, an attempt was made to use square-wave polarography. It was found that a sharp peak for In(III) was observed at −0.69 V and that the lower limit of determination was $8 \times 10^{-8}M$ (9 ppM) with respect to the original aqueous phase.

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A COMPARISON OF METHODS FOR THE DETERMINATION OF PLATINUM IN ORES

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Summary—Fire-assay and wet-extraction methods of determining platinum in ores have been evaluated. The fire-assay procedure using lead as a collector was used in combination with flame and flameless atomic-absorption, emission spectroscopy and X-ray fluorescence. In this last method flattened silver beads were analysed directly, whereas for the other methods the beads were dissolved in *aqua regia* and the solutions made up with concentrated hydrochloric acid before analysis. The wet procedures involved treatment of the ores with acids and subsequent analysis by flame atomic-absorption or by spectrophotometry after treatment with tin(II) chloride. Chromatographic, ion-exchange and solvent-extraction procedures were used to isolate platinum from base metals, the other platinum metals and gold. Results for each ore by fire assay–flame atomic-absorption, fire assay–emission spectroscopy, and wet extraction combined with spectrophotometry, showed no difference at the 99% confidence level. X-Ray fluorescence and flameless atomic-absorption results tended to be high and low respectively. The most precise method was wet extraction followed by spectrophotometric determination. Emission spectroscopy and X-ray fluorescence generally yielded the poorest precision. Wet-extraction methods were time-consuming and since no advantage was gained in accuracy over the fire-assay methods, a combined fire assay–flame atomic-absorption system was the preferred method of analysis.

An accurate determination of platinum in ores is essential. The high cost of this metal means that a relatively small error in an assay can result in a large monetary gain or loss. Early determinations for platinum included gravimetric and titrimetric methods, but as it becomes economically feasible to extract lower-grade ores, more sensitive methods of analysis must be utilized. Spectrophotometric and spectrochemical methods have now extended determinations to the microgram and in some cases even submicrogram levels.

Classically, lead was used as a collector for platinum in the fire-assay process, despite claims sometimes made that this form of collection is ineffective.[1] Other collectors[2–5] have been used, but lead still remains superior for the determination of platinum.[6] The use of a wet-extraction procedure serves as an alternative to the fire assay and provides a check on the efficiency. Wet extraction has the advantage of converting the metals into forms suitable for separational techniques such as chromatography and ion-exchange.[7]

It is the purpose of this paper to evaluate classical fire-assay and wet-chemistry procedures for the determination of platinum in ores, and to provide a comparison of the accuracy and precision to be expected for the spectrophotometric, flame and flameless atomic-absorption, emission spectroscopic, and X-ray fluorescence techniques. Results are also compared with previous analyses obtained from independent sources.

The combined fire assay–flameless atomic-absorption method, and combined fire assay–X-ray fluorescence method described in this paper have been published in greater detail elsewhere.[8,9]

EXPERIMENTAL

Apparatus

Atomic-absorption spectrophotometers. Perkin-Elmer, Model 306 and Model 403 fitted with an HGA-70 flameless atomization device and a deuterium background-corrector. Varian and Intensitron platinum hollow-cathode lamps were used.

Spectrograph. Jarrell Ash, with 3.4-m Ebert mounted grating with 5000 lines/in., giving a reciprocal linear dispersion of 0.5 nm/mm in the first order. A Jarrell Ash 21-000 non-recording densitometer was used.

X-Ray fluorescence spectrometer. University of Manitoba, Physics Department.

Spectrophotometer. Unicam SP500.

Calibrated glassware was used.

Instrumental conditions

Flame atomic-absorption

Wavelength	265.9 nm
Slit setting	4
Lamp current	25 mA
Acetylene flow-rate	3.8 l./min
Air flow-rate	24.0 l./min
Scale expansion	× 5

Burner positions and aspiration rates were adjusted for optimum absorbance each time.

Emission spectroscopy

Excitation source	Ignited a.c. arc
Primary power source	Full-wave rectified 230-V, 60-Hz power supply, initiated by a high-voltage condensed spark synchronized to initiate each half-cycle.

Radiofrequency current	2.0 A
Capacitance	0.0025 μF
Inductance	15 μH (residual)
Discharge voltage	2400 V
Arc current	7.5 A
Slit-width	20 μm
Analytical gap	3 mm
Transmission*	Steps 1 and 2 of a 7-step filter
Exposure	20 sec
Emulsion	Kodak SA-1
Electrodes	Anode—ASTM 8 (flat end)
	Cathode—ASTM 5 (flat end)
X-Ray fluorescence	
Tube	Molybdenum
Voltage	40 kV
Filament current	20 mA
Detector	Kevex Si(Li) with an active area of 30 mm^2 and resolution of 195 eV full-width at half maximum (FWHM) at 5.9 keV
Counting time	8 min

X-Rays from the molybdenum tube are filtered (5-mm Mo foil) so as to be largely monochromatic, collimated and allowed to fall on the sample. The Si(Li) detector is placed immediately below the sample out of the path of the main beam and operated at the temperature of liquid nitrogen. The detector output signals are amplified and shaped for sorting by a 1024-channel pulse-height analyser. The memory of the pulse-height analyser may be continuously monitored by a display oscilloscope, allowing the entire range to be inspected at a single glance. The data are recorded in digital form as a teletype read-out of the memory of the analyser.

Flameless atomic-absorption

Wavelength	265.9 nm
Slit setting	4
Lamp current	28 mA
Drying time	40 sec
Charring time	35 sec
Atomization time	15 sec
Drying temperature	100°
Charring temperature	1100°
Atomization temperature	2600° (10 v)
Water flow	3 l./min
Argon flow	3–5 arbitrary setting
Chart speed	51 mm/min
Sample volume	50 μl

Several graphite tubes were used in this work. They had been used to some extent before the platinum injections. Before each analysis, the tube was fired to maximum temperature for 2–3 sec. The platinum solutions were then injected. In all cases consistent results were obtained immediately.

Reagents

Platinum solution (1 mg/ml). Dissolve 1 g of pure platinum wire in *aqua regia.* Remove nitrous oxides by repeated evaporation with concentrated hydrochloric acid. Filter into a 1-litre flask, washing and making up to volume with 0.1*M* hydrochloric acid. Standardize with thiophenol,[10] or spectrophotometrically.[11]

Palladium and gold solutions (1 mg/ml). Dissolve 1 g of the pure metal in *aqua regia,* evaporate several times with concentrated hydrochloric acid and make up to volume in 0.1*M* hydrochloric acid.

* Neutral filters with deposited aluminium bands of different transmittance placed at the slit of the spectrograph. Prepared at A.E.C.L. Pinawa, Manitoba. Transmission of step 1 is 100% and of step 2 is 62.1%.

Rhodium solution (1 mg/ml). Dissolve 0.5838 g of sodium hexachlororhodate in 100 ml of 0.1*M* of 0.1*M* hydrochloric acid.

Iridium solution (1 mg/ml). Dissolve 0.7292 g of sodium chloroiridate in 100 ml of 0.1*M* hydrochloric acid.

Silver nitrate solutions (2 and 20 mg/ml). Dissolve 0.3148 and 3.148 g of silver nitrate in 100 ml of doubly distilled, doubly demineralized water.

Lead. Foil, 0.004-in. thick.

Stannous chloride solution. Dissolve 19 g of stannous chloride in 100 ml of 3*M* hydrochloric acid.

Lanthanum chloride solution. Dissolve 6.45 g of lanthanum oxide in 100 ml of 6*M* hydrochloric acid.

Molybdenum chloride solution. Dissolve 0.15 g of molybdenum trioxide in 100 ml of 3*M* hydrochloric acid.

Tri-n-butyl phosphate. Equilibrated with 6*M* hydrochloric acid before use.

Buffer solution. Mix 50 ml of 4*M* sodium acetate with 53 ml of 4*M* hydrochloric acid to give a solution of pH 2.2 ± 0.2.

Cation-exchange resin. Bio-Rad AG 50W X 8 analytical grade, 50-mesh, hydrogen form.

Porasil C. Waters Associates, Inc., 80–100 mesh.

Preparation of chromatographic columns

Bio-Rad AG 50W-X8. The resin was cleaned by gentle heating with 50% v/v hydrochloric acid and washed several times by decantation with water. The ion-exchange column (2.5 × 40 cm) was filled to a height of 25 cm with the resin and the resin was washed with water until the pH of the eluate was the same as that of the water.[7] After use, the resin was regenerated with 35% v/v hydrochloric acid and again washed until the pH of the eluate was the same as that of the water. The small cation-exchange column was 1.2 × 30 cm filled to a height of 10 cm.

Porasil C treated with tri-n-butyl phosphate. TBP (5 g) dissolved in chloroform was added to 15 g of Porasil C that had previously been washed with concentrated hydrochloric acid, then with water, and finally dried. The slurry was stirred to remove most of the chloroform, and then left overnight in a drying oven at 75°. Some of the TBP-treated Porasil C (1.5 g) was transferred to a glass column (1.2 × 30 cm) with water, and conditioned with 10 ml of 0.1*M* hydrochloric acid before use.[12]

Ores

The ores were obtained from the Merensky Reef in the Bushveld Igneous Complex, South Africa. The major component of such ores is pyroxene [silicates of calcium, magnesium, iron, aluminium and lithium, mainly bronzite $(Mg,Fe)_2Si_2O_6$]. Minor components include chromite $[Fe(Cr,Fe)_2O_4]$, chalcopyrite ($CuFeS_2$), pyrrhotite (FeS) and pentlandite $[(Fe,Ni)_9S_8]$. Trace constituents include a variety of sulphides of iron, copper and nickel. Platinum metals are present as native platinum, sperylite ($PtAs_2$), braggite (Pt_2PdNiS_4), stibiopalladinite (Pd_3S_6), copperite (PtS), and laurite (RuS_2). A proportion of the platinum metals is also present in solid solution in the sulphides of iron, copper and nickel. Each ore, designated by name or number, had previously been analysed for the platinum metals and gold.[13,14] Results for platinum, together with the methods of analysis, are shown in Table 1. The results quoted for USBM 31 are from laboratories taking part in a "round-robin" analysis. The values rejected in averaging were rejected by the U.S. Bureau of Mines. Where possible, precision has been quoted at the 95% confidence level.

Fire assay of ores

The procedure used was developed in this laboratory from various methods.[7] Ores received in this laboratory had been crushed to pass sieves of 100 and 200 mesh. The entire ore sample, weighing 1–2 lb, was placed on

Table 1. Previous analyses of ores for platinum

Method	Concentration of platinum, *ppm* S4[10]	Float concentrate[10]	USBM 31[11]
Fire assay and flame atomic-absorption	5.23	82.60	5.04 ± 0.17
Fire assay and flame atomic-absorption			8.1*
Fire assay and flame atomic-absorption			2.1*
Fire assay and emission spectrography			4.6 ± 1.0
Fire assay and emission spectrography			5.04 ± 0.28
Fire assay and emission spectrography			4.78 ± 0.96†
Fire assay and emission spectrography			5.1 ± 0.2
Fire assay and emission spectrography			3.4*
Fire assay and spectrophotometry			4.63
Fire assay and spectrophotometry			4.5 ± 0.2
Fire assay and spectrophotometry			5.61 ± 0.32
			Average = 4.9

* Not included in average value for platinum.
† No confidence limits quoted.

a large cellophane sheet and rolled or tumbled by lifting alternate corners of the sheet. After 25 min of mixing, the ore was spread out evenly and marked off into 2.5-cm squares. The sample for assay was then obtained by taking small portions from each square with a spatula, with care taken to ensure that the spatula reached the bottom of the square. With practice, approximately equal portions could be taken from each square, thus keeping variations to a minimum. This procedure was repeated to obtain ore samples for further assays except that the rolling and tumbling was reduced to 5 min.

The ore samples were then added to small polyethylene bags containing 85 g of PbO, 21.1 g of Na_2CO_3, 4.5 g of CaO and 2 g of flour. Depending on the weight of ore, various amounts of silica were added so that the flux was not too basic. Silica (15 g) was used as a blank ore. The "float concentrate" and USBM 31 were roasted in air for 1 hr at 700° before being added to the flux. A known amount of silver, in the form of silver nitrate solution, was added to each flux. Each bag was placed in a crucible pot and the pots were placed in a drying oven at 70° for several hours. After the drying, lumps were broken up and the mixture was thoroughly shaken for 4–5 min.

The crucible pots were placed in the furnace at 950° and raised to 1200° at the maximum heating rate of the furnace. This normally required 75–90 min. After 15 min at this temperature, the pots were removed from the furnace and the molten contents poured into conical iron moulds. When cool, the slags could be separated from the lead buttons by gentle tapping with a small hammer.

The lead buttons were added as quickly as possible to magnesia cupels placed in the furnace at 960°; the cupels had been heated for at least 10 min before use. The furnace door was kept closed for 5 min to allow the lead to melt and then kept open with a 0.6-cm thick steel plate under it. Under these conditions the driving of the lead occurred at a rate of approximately 1 g/min. When the driving was complete, the furnace door was closed and cupellation continued for a further 5 min. The cupels were then slowly withdrawn from the furnace and allowed to cool. The silver beads were then analysed for their platinum content by the methods outlined below.

Flame atomic-absorption

Silver beads weighing 6 mg, obtained from the fire assay of approximately 15 g of S4 and 11 g of USBM 31, were placed in 10-ml standard flasks containing 0.5 ml of concentrated nitric acid. The flasks were immersed in hot water until dissolution of the silver was complete. Concentrated hydrochloric acid (3.75 ml) was added and heating continued to dissolve the platinum. The flasks were cooled, usually overnight, 2 ml of lanthanum chloride solution were added and the solutions made up to volume with distilled water. Platinum absorbances were measured by running a lower concentration standard, followed by two samples and a higher concentration standard in quick succession. Standards were prepared by adding μl quantities of stock solutions of platinum and silver nitrate, 2 ml of lanthanum chloride solution and the required amounts of concentrated nitric and hydrochloric acids to 10-ml standard flasks and making up to volume.

Silver beads, weighing 25 mg, obtained from the fire assay of approximately 8 g of float concentrate were added to 25-ml standard flasks and dissolved acid in the manner described above, with enough of the reagents to give the same final concentrations. Lanthanum concentration was maintained constant by adding 5 ml of the lanthanum chloride solution.

Results from these analyses are shown in Table 2.

Emission spectroscopy

The method was developed by the A.E.C.L. at Pinawa, Mantoba, from a procedure by Haffty and Riley.[16] Silver beads, weighing 20 mg, were placed in 25-ml standard flasks containing 0.5 ml of concentrated nitric acid. The flasks were immersed in hot water to encourage dissolution

Table 2. Analysis of ores by combined fire assay and flame atomic-absorption

Concentration of platinum, *ppm* S4	Float concentrate	USBM 31
5.21	79.2	5.73
5.78	79.6	5.84
5.36	81.8	5.03
4.91	80.0	5.30
4.59*	78.3	5.39
5.03	79.9	5.95
4.93	78.6	5.83
5.37	79.3	5.07
5.47	77.5	
5.51	85.2*	
5.07	81.2	
Averages: 5.26 ± 0.20†	79.5 ± 0.9†	5.52 ± 0.31†

* Values rejected at the 95% confidence level.
† ± values quoted at the 95% confidence level.

Table 3. Analysis of ores by combined fire assay and ignited a.c. arc

Concentration of platinum, *ppm*		
S4	Float concentrate	USBM 31
5.67	78.9	5.98
4.76	79.4	4.38
4.79	84.7	6.10
5.60	78.8	4.52
6.02	69.6	4.03
6.04	71.2	5.09
5.79	77.2	4.79
4.76		
Averages: 5.43 ± 0.49†	77.1 ± 5.0†	4.98 ± 0.73†

† ± values quoted at the 95% confidence level.

Table 4. Analysis of ores by combined fire assay and X-ray fluorescence

Concentration of platinum, *ppm*		
S4	Float concentrate	USBM 31
5.45	90.8	5.19
4.54	92.0	8.26
6.02	80.3*	6.88
6.32	89.0	6.74
4.97	90.6	6.08
5.59	92.6	6.23
4.29		7.04
		6.01
Averages: 5.31 ± 0.69†	91.0 ± 1.7†	6.55 ± 0.75†

* Value rejected at the 95% confidence level.
† ± values quoted at the 95% confidence level.

of the silver, 2 ml of concentrated hydrochloric acid were added and the heating continued until the platinum was dissolved. To the cooled solutions, 40 μl of 1000-ppm molybdenum solution were added and the solutions were made up to volume with concentrated hydrochloric acid. Then 200 μl were added in 50-μl portions to the flat end of an electrode that had first been waterproofed with 20 μl of 1% solution of polystyrene in benzene; each portion was evaporated to dryness under a heat lamp before the next was added. A final 20-μl portion of polystyrene solution was applied before arcing.

The residues were excited with an ignited a.c. arc for 20 sec. Photographic plates were calibrated with an iron spectrum excited with a d.c. arc at 7 A for 8 sec, with a slit-width of 20 μm. The intensities of the Pt 306.471 and Mo 281.615 nm lines were measured and the intensity ratio was used to determine the amount of platinum, from a calibration curve.

Standards were prepared by cupelling lead boats containing 0 (blank), 10, 20, 40, and 60 μg of platinum to give 20-mg silver beads. Solutions of each bead were prepared as described above and a calibration curve was drawn from the results for each standard run in triplicate.

Several plates were used to accommodate all the ore samples and cupellation standards were run on each plate to check the calibration.

Ore weights were such that between 20 and 50 μg of platinum were present. Results are shown in Table 3.

X-Ray fluorescence[9]

Silver beads, weighing approximately 11 mg, were flattened between two steel blocks in order to present as large a surface area as possible to the X-ray beam. This was accomplished in two stages: after cupellation any adhering cupel material was carefully scraped away with a spatula and the beads were flattened till about 0.5 mm thick; the beads were then annealed by heating in a porcelain crucible at red heat for 2–3 min, and finally flattened under weight of 10 tons with a hydraulic press. The bead thickness was 0.10–0.12 mm; the diameters were 3.70–4.10 mm.

The beads were mounted on "Mylar" foil (450 μg/cm^2) stretched over aluminium foil and held in position by vacuum grease. The holder was placed in the specimen chamber, which was then evacuated. The sample was at 45° to the beam. Each bead was counted for 8 min. The intensity ratio $Pt_{L\alpha}/Ag_{K\alpha}$ was measured and the percentage of platinum read from a calibration curve.

Standards were prepared by salting lead boats with 0.18–4.2% of platinum and cupelling to give 11-mg silver beads. Standard beads (21 in all) were prepared in triplicate for each concentration. The concentration of platinum in the beads was calculated from the weights of the platinum added and of the bead after cupellation. $Pt_{L\alpha}$ intensities were corrected for blank values; no correction was applied to the $Ag_{K\alpha}$ line. The calibration curve was drawn by using the method of least squares.

The weights taken of ores S4 and USBM 31 were such that a minimum of 40 μg of platinum was determined. For the float concentrate 1–2 g was taken. Results are shown in Table 4.

Flameless atomic-absorption[8]

Silver beads, weighing 2 mg, obtained from the fire assay of ores S4 and USBM 31 were added to 10-ml standard flasks containing 0.5 ml of concentrated nitric acid. The flasks were placed in hot water as before, 5 ml of concentrated hydrochloric acid were added and heating continued until the platinum had dissolved. After cooling the solutions were diluted to volume with distilled water.

Silver beads weighing 20 mg, obtained from the fire assay of the float concentrate were added to 100-ml standard flasks and dissolved in the same way, with ten times as much acid, and the solutions diluted to volume.

Ore samples and standards were analysed with 2 or 3 samples being fired between standards. Ore samples were chosen at random for each firing. Standards were prepared by adding μl quantities of stock solutions of platinum and silver nitrate to 10-ml standard flasks and making up to give 5% v/v nitric acid and 50% v/v hydrochloric acid in the final solution. The calibration curve was drawn by the least-squares method.

The weights taken were 1–2 g of float concentrate and 3–7 g of S4 and USBM 31.

Results are shown in Table 5.

Table 5. Analysis of ores by combined fire assay and flameless atomic-absorption

Concentration of platinum, *ppm*		
S4	Float concentrate	USBM 31§
5.43	77.0	4.56
4.61*	143.5*	4.25
5.61	103.7*	4.88
5.61	76.2	5.04
5.50	68.2	4.25
5.58	71.9	4.69
5.46	78.4	4.28
4.92	73.2	4.63
Averages: 5.44 ± 0.22†	74.2 ± 4.0†	4.57 ± 0.28†

* Values rejected at the 95% confidence level.
† ± values quoted at the 95% confidence level.
§ Average of at least 3 injections.

Wet extraction for ores[1,7,12]

After roasting at 700° for 1 hr, the float concentrate samples (weighing 3–7 g) were placed in Nalgene beakers and each treated with three 25-ml portions of hydrofluoric acid, followed by three 25-ml portions of *aqua regia*, followed finally by three 25-ml portions of concentrated hydrochloric acid, with evaporation to dryness on a steam-bath after each addition, and with stirring at frequent intervals. Finally 25 ml of concentrated hydrochloric acid were added to each, followed by 25 ml of water, and the solutions were filtered (Whatman No. 42 paper) into 200-ml beakers. The papers and residues were washed well with hot 1*M* hydrochloric acid. The solutions were evaporated to dryness on a steam-bath and 50 ml of 0.1*M* hydrochloric acid added to each. Residual silica was filtered off, and the solution (plus washings) was passed through the TBP-treated Porasil C column at the maximum rate of the column, into a 400-ml beaker, the column being washed with 0.1*M* hydrochloric acid until the total volume was about 300 ml. This solution was passed through a Bio-Rad 50W-X8 cation-exchanger at a rate of 1 drop/sec. The cation-exchanger was washed free from platinum metals with 150–200 ml of 0.1*M* hydrochloric acid. The solution was evaporated to dryness on a steam-bath after the addition of 25 ml of concentrated hydrochloric acid.

Concentrated hydrochloric acid (2 ml), 72% perchloric acid (15 ml) and concentrated nitric acid (5 ml) were added and the mixture was gently boiled for 15 min to remove organic matter. This treatment also served to remove osmium and ruthenium, if present, as the tetroxides. The mixture was then slowly evaporated to dryness and the salts were boiled with concentrated hydrochloric acid to convert the platinum metals into their respective chloro-complexes. The solution was evaporated to dryness and the treatment with concentrated hydrochloric acid repeated twice more. The platinum metal salts were finally dissolved in a small amount of water, the solution was filtered through Whatman No. 541 paper and washed with water into a 25-ml standard flask containing 5 ml of lanthanum chloride solution. The solutions were analysed for platinum content by flame atomic-absorption, by first aspirating a standard of lower platinum concentration, followed by two ore samples, and finally a standard of higher platinum concentration. Standards were prepared with the same amount of lanthanum solution and known concentrations of platinum obtained by dilution of a stock solution. Reagent blanks were put through the method but no platinum was detected. The results of these analyses are shown in Table 6.

The float concentrate residues were fire-assayed, with the carbon content of the filter papers taken into account. The silver beads obtained were analysed by flame atomic-absorption, but no platinum was detected.

Samples of ores S4 and USBM 31 (5–10 g) after roasting at 700° for 1 hr were treated similarly to the float concentrate samples until after the passage through the cation-exchange column. On evaporation of the effluents from the cation-exchanger, a white precipitate settled out at low volume and the solutions turned green. Repeated filtrations failed to remove the precipitate, identified as silica by X-ray fluorescence, and so an additional evaporation step with 3–4 ml of hydrofluoric acid was included in the analytical scheme.

The green solid obtained on evaporating to dryness was found to contain chromium (by the diphenylcarbazide test) and this was confirmed by atomic absorption. Also, on boiling with perchloric acid, the solution turned red and a red solid precipitated on cooling; this is further evidence of chromium.[17] Chromium(III) is oxidized to chromium(VI) which is precipitated in cold perchloric acid. On evaporation of the perchloric acid and addition of hydrochloric acid, the chromium(VI) is reduced to chromium(III), giving the green colour. Repeated passage through the cation-exchanger failed to remove the chromium(III), but its presence was not detrimental because it is not extracted into TBP,[18] and so is not likely to interfere in the platinum determination.[19] Hence, the platinum was determined without any further attempts at removal of chromium(III).

After treatment with hydrofluoric acid, each residue was evaporated to dryness several times in the presence of concentrated hydrochloric acid. Organic matter was removed by boiling with a mixture of hydrochloric, perchloric and nitric acids. The mixture was then slowly evaporated to dryness and the residue again treated several times with concentrated hydrochloric acid, with evaporation to dryness each time. The residue was dissolved in 10 ml of 6*M* hydrochloric acid and the solution transferred to a 60-ml separatory funnel with an additional 10 ml of acid. The solution was shaken with 5 ml of 4% sodium iodide solution and the mixture allowed to stand for at least 10 min. The iodo-complexes of platinum and palladium were then extracted with two 15-ml portions of 15% TBP solution in hexane. The aqueous layer was washed with 10 ml of hexane and the hexane portion added to the combined TBP extracts. The aqueous phase, containing iridium and rhodium, was discarded.

The combined TBP extracts were shaken with three 10-ml portions of concentrated nitric acid for 30 sec each time. The combined acid extract was diluted with an equal volume of water and washed with 10 ml of hexane. The organic phases were discarded. The acid solution was evaporated to dryness on a steam-bath after addition of 1 ml of 5% sodium chloride solution. Platinum and palladium were converted into their chloro-complexes by repeated evaporation with concentrated hydrochloric acid. Two ml of buffer solution and 10 ml of water were added and the solution was warmed to dissolve the residue, then cooled to room temperature. One ml of 0.5% solution of *p*-nitrosodimethylaniline in alcohol was added and the solution transferred to a 60-ml separatory funnel with the minimum of water. The red palladium complex was extracted with two 15-ml portions of chloroform and discarded. The aqueous layer was filtered through Whatman No. 541 paper into a 200-ml beaker and the paper was washed with water. Approximately 2 ml of concentrated sulfuric acid and 5 ml of perchloric acid were added and the mixture was evaporated to fuming (until only 2–3 ml were left). The mixture was quickly cooled by immersion of the beaker in cold water, and then added to a 25-ml

Table 6. Analysis of ores by wet extraction

Concentration of platinum, *ppm*			
S4	Float concentrate	USBM 31§	
5.09[a]	80.1[b]	5.78[a]	4.90[b]
5.19	82.3	5.92	4.28
4.51*	82.4	4.20	4.21
5.15	84.6*	5.40	5.35
5.37	81.9	5.30	
5.11	80.2	5.14	
5.30	81.8	3.92	
	81.2		
	79.8		
	79.1		
	80.2		
Averages: 5.20 ± 0.12†	80.9 ± 0.8†	4.95 ±0.46†	

[a] Spectrophotometric determination.
[b] Flame atomic-absorption determination.
* Values rejected at the 95% confidence level.
† ± values quoted at the 95% confidence level.
§ Results quoted are for wet extraction of ores followed by fire assay of residues.

standard flask containing 5 ml of stannous chloride solution. Platinum was determined spectrophotometrically at 400 nm, in 4-cm cells. Reagent blanks were also carried through the procedure. Results are recorded in Table 6.

The residues from the acid extractions were fire-assayed. The silver beads obtained from cupellation were dissolved in *aqua regia* and the solutions evaporated to dryness. Residues were treated several times with concentrated hydrochloric acid and finally dissolved in 0.1*M* hydrochloric acid. The solutions were filtered to remove silver and lead, the filters washed with 0.1*M* hydrochloric acid, and the solutions then analysed for platinum in the same way as the ore samples except that the small cation-exchange column was used. No platinum was recovered from USBM 31. The results quoted in Table 6 for USBM 31 are therefore for a combined fire assay and wet extraction procedure.

In another experiment two USBM 31 ore samples were boiled with perchloric acid for 3 hr before the usual acid treatment (perchloric acid is frequently used for dissolution of chromium ores).[17] However, low results were again obtained and the ore residues still had to be fire-assayed for complete recovery.

Analyses of USBM 31 were obtained without using the solvent-extraction procedure, by atomic-absorption measurements directly on the solutions after passage through the cation-exchange column. Chromium is known to cause interference in the atomic-absorption determination of platinum when present in the ratio 50:1 (Cr:Pt), even in the presence of releasing agents.[20] Thus, it was deemed necessary to try to remove as much of the chromium as possible before final determination. This was done by adding concentrated hydrochloric acid in 2 or 3 portions to the hot solution in perchloric acid, to volatilize chromium as chromyl chloride.[21] The addition was repeated until no more chromyl chloride was evolved.

It was assumed that platinum was not volatilized under these conditions. Platinum metals were converted into their chloro-complexes by repeated evaporation with concentrated hydrochloric acid, dissolved in water and finally transferred to 10-ml standard flasks containing 2 ml of lanthanum chloride solution. Results are shown in Table 6. Recoveries were still low and ore residues had to be fire-assayed for complete recovery. Twice as much ore as usual was used for this analysis.

RESULTS AND DISCUSSION

The results obtained for the analysis of each ore and the precision obtained by each method are summarized in Table 7. These results are compared with values obtained independently as described in Table 1. Good agreement with previous analyses is demonstrated for each ore, except for X-ray fluorescence of the float concentrate and USBM 31, and flameless atomic-absorption of the float concentrate.

The Student *t*-test was used to determine if there was any difference in the averages obtained by the different procedures for each ore. Results obtained for S4 are not statistically different at the 95% confidence level. For the float concentrate and USBM 31, flame atomic-absorption and emission spectrographic results are the same at the 95% confidence level, and are the same as for wet extraction, at the 99% confidence level. The results obtained by X-ray fluorescence and flameless atomic-absorption for the float concentrate and USBM are respectively high and low, although the flameless atomic-absorption result for USBM 31 shows no statistical difference at the 95% level from the results obtained by emission spectroscopy and wet extraction. The reason for these high and low values is not readily apparent, especially in light of the excellent agreement obtained by both methods for S4.

Several generalizations may be made about the precision obtained by each method. Emission spectroscopy and X-ray fluorescence yield lower precision. This is due in part to the difficulty in preparing standards with platinum contents known to a high degree of accuracy. Precision for S4 and USBM 31 (of which approximately equal amounts were taken) is fairly constant except for analysis by wet extraction and spectrophotometry. The large difference may be attributed to the nature of the ores. Recovery of platinum was complete for S4 by wet extraction, but USBM 31 required fire assay of the residue after acid extraction to effect complete recovery. Flameless atomic-absorption shows precision close to that of flame atomic-absorption for S4 and USBM 31. The most precise method was wet extraction followed by spectrophotometry. The precision obtained in this study by flame atomic-absorption, emission spectroscopy and spectrophotometry compares favourably with that obtained in the previous analysis of USBM 31 (Table 1). Emission spectroscopy tends to give lower and more variable precision than the other two techniques, as can be seen from the previous analyses of USBM 31 listed in Table 1. The precision obtained in the present study is approximately equal to the average for the four results in Table 1.

The precision obtained for emission spectroscopy in this study may be improved by using smaller bead weights and diluting to smaller volumes, resulting in more platinum being applied to the electrode, in the same volume taken from the sample solution.

The use of an ignited a.c. arc requires an explanation. Initially, 20-mg silver beads were placed in standard $\frac{3}{16}$-in. cupped graphite electrodes with 6 mg of lithium fluoride added as a buffer to prevent bead ejection during arcing. The beads were excited by means of a d.c. arc (11.5 A) in an argon–oxygen atmosphere, followed by three photographic exposures. Exploratory results gave a linear log–log plot of concentration of platinum *vs.* intensity of the 306.471 nm spectral line. Hence, all beads to be used in further emission spectrographic work were prepared so that they contained 20 mg of silver. Beads to be used as standards were prepared by cupellation, and ore beads by fire assay.

Arcing of these beads failed to reproduce the linear relationship found in the exploratory work. Indeed, in some cases, no platinum was found at all. Close examination of the beads during arcing showed that after all the silver had volatilized, platinum was left on the electrode in the form of a "leaf". This leaf either burnt to completion or was ejected at random intervals, causing erratic results. Copper powder was

Table 7. Comparison of the accuracy and precision of the methods used

Method of analysis	S4				Float concentrate				USBM 31			
	Average, ppm	σ ppm	No. of values	C.V., %	Average, ppm	σ ppm	No. of values	C.V., %	Average, ppm	σ, ppm	No. of values	C.V., %
Fire assay and flame atomic-absorption	5.26	0.20	10	3.8	79.5	0.9	10	1.2	5.52	0.31	8	5.6
Fire assay and emission spectroscopy	5.43	0.49	8	9.0	77.1	5.0	7	6.5	4.98	0.73	7	14.6
Fire assay and X-ray fluorescence	5.31	0.69	7	13.0	91.0	1.7	5	1.9	6.55	0.75	8	11.5
Fire assay and flameless atomic-absorption	5.44	0.22	7	4.0	74.2	4.0	6	5.4	4.57	0.28	8	6.1
Wet extraction	5.20*	0.12	6	2.3	80.9†	0.8	10	1.0	4.95§	0.46	11	9.3
Independent analysis	5.23				82.6				4.9		8	

σ = Standard deviation at the 95% confidence level.
C.V. = Coefficient of variation.
* Spectrophotometric determination.
† Flame atomic-absorption.
§ Grand average of spectrophotometric and flame atomic-absorption results.

added to the electrode to try to prevent platinum ejection. Copper electrodes have successfully been used for arcing silver beads.[22] However, copper failed to overcome the problem, ejection still taking place after the volatilization of the copper. Reduction of the arc current to 7 A also proved unsuccessful. This line of work was discontinued and silver beads were dissolved and applied to the electrodes as solutions.

Aliquots were applied to the flat end of the electrode as described, and the electrode was then mounted against a conically tipped graphite electrode and arced at 11.5 A in an argon–oxygen atmosphere with an analytical gap of 4 mm. A 45-sec preburn followed by a 35-sec exposure was used. Results were very erratic, especially at low loadings of platinum, *e.g.*, 80 ng. Precision at this level, with the Pt 265.945 and 306.471 nm lines, was ±50%. This may have been due to the fact that 80 ng was near the detection limit. Internal standardization was not attempted. Most of the elements considered were volatilized before platinum during the preburn, and those that would have been usable, the platinum metals and gold, were unsuitable because of their presence in the ore samples. However, internal standardization was not considered essential, since the arc burned very quietly and steadily with minimum wandering and was constantly focused on the slit.

Because of the lack of success with a d.c. arc it was decided to utilize the method of Haffty and Riley,[16] and use an ignited a.c. arc to excite the platinum. For this method 40 μl of molybdenum solution were added to each solution. Standard solutions were prepared by pipetting μl quantities of stock platinum and silver solutions, together with 40 μl of molybdenum solution, into 25-ml standard flasks and adding the required amount of nitric and hydrochloric acids.

The results obtained for the ore and synthetic fire-assay beads by using the intensity ratio of the Pt 265.945 and Mo 281.615 nm lines were 30–50% lower than those obtained with the calibration graph obtained with standard platinum solutions. When cupellation beads were used as calibration standards, however, the results indicated quantitative recovery of platinum. Because the other methods of analysis in this study show that the fire-assay and cupellation steps are essentially quantitative for platinum, the only tentative explanation to be offered is that some interference introduced during one of these common steps must reduce the emission intensity.

The analysis of USBM 31 by X-ray fluorescence was high compared with the previous analyses. Bead homogeneity was tested by counting the opposite side of each bead. The result of this analysis was 6.36 ± 0.60 ppm, indicating homogeneity. The beads were also examined for lead. Lead peaks appear on the short wavelength side of the platinum peaks and hence may cause enhancement of the platinum–silver ratio. No evidence of lead was found. Also, from experience with lead beads, more lead is usually found

on the surface attached to the cupel, and so enhancement should be much higher on one side of the bead than on the other; this was not the case. Thus no satisfactory explanation can be given for the high result.

X-Ray fluorescence offers the advantages that the samples are not destroyed and the potentially variable photographic processes are eliminated. Precision may be increased by longer counting times or by using a crystal spectrometer and obtaining higher count rates in a shorter time. Sensitivity may also be increased by the use of higher energy X-ray tubes.

For low values of platinum, flameless atomic-absorption and emission spectroscopy have been shown to offer feasible alternatives to spectrophotometric determinations when highest accuracy and precision are not required.

Although the most precise method was wet extraction followed by spectrophotometric determination for S4, wet-extraction procedures are very time-consuming and no advantage in accuracy is gained over fire assay. For spectrophotometric determinations the removal of the other platinum metals and gold is essential because they all interfere in the stannous chloride method. Gold was removed in the float concentrate analysis because under certain conditions it exhibits erratic behaviour on cation-exchange columns,[23] and it was felt that this could affect the recovery of platinum. This hypothesis is purely speculative and no results are produced to support it.

When the platinum concentration is large enough, fire assay followed by flame atomic-absorption is the preferred method of analysis. While it may be fortuitous that the ores chosen for this study were amenable to fire assay, the results indicate that when this is the case, the method may be used on a routine basis. Wet extraction provides an independent method for evaluating the fire-assay procedure and is especially useful when fire-assay values are in doubt. Though this method is time-consuming it requires less knowledge of ore composition than is needed for fire assay. However, it is sometimes necessary, as shown in the case of USBM 31, to fire-assay the residues for highest accuracy.

To the authors' knowledge, this is the first time that flameless atomic-absorption, emission spectrographic and X-ray fluorescence techniques have been compared for determination of platinum in ores.

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DETERMINATION OF ANTIMONY IN CONCENTRATES, ORES AND NON-FERROUS MATERIALS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY AFTER IRON–LANTHANUM COLLECTION, OR BY THE IODIDE METHOD AFTER FURTHER XANTHATE EXTRACTION

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Summary—Methods for determining trace and moderate amounts of antimony in copper, nickel, molybdenum, lead and zinc concentrates and in ores are described. Following sample decomposition, antimony is oxidized to antimony(V) with *aqua regia*, then reduced to antimony(III) with sodium metabisulphite in 6*M* hydrochloric acid medium and separated from most of the matrix elements by co-precipitation with hydrous ferric and lanthanum oxides. Antimony (≥ 100 μg/g) can subsequently be determined by atomic-absorption spectrophotometry, at 217.6 nm, after dissolution of the precipitate in 3*M* hydrochloric acid. Alternatively, for the determination of antimony at levels of 1 μg/g or more, the precipitate is dissolved in 5*M* hydrochloric acid containing stannous chloride as a reductant for iron(III), and thiourea as a complexing agent for copper. Then tin is complexed with hydrofluoric acid, and antimony is separated from iron, tin, lead and other co-precipitated elements, including lanthanum, by chloroform extraction of its xanthate. It is then determined spectrophotometrically, at 331 or 425 nm, as the iodide. Interference from co-extracted bismuth is eliminated by washing the extract with hydrochloric acid of the same acid concentration as the medium used for extraction. Interference from co-extracted molybdenum, which causes high results at 331 nm, is avoided by measuring the absorbance at 425 nm. The proposed methods are also applicable to high-purity copper metal and copper- and lead-base alloys. In the spectrophotometric iodide method, the importance of the preliminary oxidation of all of the antimony to antimony(V), to avoid the formation of an unreactive species, is shown.

For use in the Canadian Certified Reference Materials Project, a method was required for the determination of antimony in concentrations as low as 1 μg/g. Recent work by the author on the extraction of metal ethyl xanthate complexes from hydrochloric acid media[1] has resulted in methods for determining tellurium[2] and arsenic[3] in copper, lead, zinc, nickel and molybdenum concentrates. These methods are based on the co-precipitation of tellurium(VI) and arsenic(V) with hydrous ferric oxide from an ammoniacal medium, followed by their separation from iron by chloroform extraction as the xanthates from $\geq 11M$ hydrochloric acid media. It is known that antimony can also be separated by the same co-precipitation procedure[4,5] and that antimony(III) can be quantitatively extracted as the xanthate from acid media.[1,6] Therefore, it was considered that a similar method might be developed for antimony.

Probably the most common methods currently used for determining antimony involve atomic-absorption finishes, often after prior separation of antimony by co-precipitation[7–10] or extraction techniques.[11,12] However, these methods are not sensitive enough for the determination of μg-quantities of antimony. More sensitive atomic-absorption methods, based on hydride-evolution techniques, have been reported but these are subject to numerous interferences.[13,14] The most widely used spectrophotometric methods involve the formation and extraction of the ion-association complexes formed between the chloro-complex of antimony(V) and xanthene or basic triphenylmethane dyes[15,16] such as Rhodamine B[17,18] or Brilliant Green,[19,20] respectively, followed by direct measurement of the absorbance of the extract. Although these methods are sensitive (molar absorptivities up to $\sim 1 \times 10^4$ l.mole^{-1}.mm^{-1}), they are not very specific because other elements that form chloro-complexes react in a similar manner.[15,16] Furthermore, reproducibility is generally poor because the methods are based on the reaction of antimony(V), which rapidly hydrolyses to form unreactive compounds in the strongly acidic chloride medium required for the oxidation of antimony and for the extraction of the complex.[21–23] Reasonably reproducible results can be obtained only if the time interval after the oxidation step, and before the extraction step, is rigidly controlled.[17,19,20,23]

Recently, the author reported the determination of

bismuth at the μg/g-level by the iodide method, after its separation by diethyldithiocarbamate and xanthate extractions.[24] In this work, the sensitivity of the method was increased about threefold by measuring the absorbance of the complex at the wavelength of maximum absorption (337 nm) in the near ultraviolet. Because antimony(III) [and antimony(V) which is reduced by iodide] forms a similar stable iodide complex in dilute sulphuric acid media, and because the sensitivity of the method can be increased about sevenfold, *i.e.*, to 3.11×10^3 $l.mole^{-1}.mm^{-1}$, by measuring the absorbance at 331 nm,[25] the wavelength of maximum absorption, this simple and sensitive spectrophotometric finish was also chosen for use in the present work.

This paper describes both a spectrophotometric and an atomic-absorption method for the determination of antimony in copper, lead, zinc, nickel and molybdenum concentrates, and in ores, high-purity copper metal and copper and lead-base alloys. Both methods involve the preliminary separation of antimony(III) from most of the matrix elements by coprecipitation with hydrous ferric and lanthanum oxides. The spectrophotometric method, which is based on the ultimate formation of antimony(III) iodide, involves further separation of antimony by chloroform extraction as the xanthate from a 5*M* hydrochloric acid medium containing tartaric and hydrofluoric acids, stannous chloride and thiourea. Antimony is subsequently separated from co-extracted bismuth by washing the extract with hydrochloric acid of the same acid concentration as the medium used for extraction. An advantage of the proposed spectrophotometric method over those based on separations involving the extraction of the antimony(V) chloro-complex,[11,12] or similar coloured ion-association dye complexes, is that the xanthate extraction step involves antimony(III) which is stable in acidic chloride media.

EXPERIMENTAL

Apparatus

All results by atomic-absorption spectrophotometry were obtained with a Varian Techtron model AA6 spectrophotometer equipped with a 10-cm laminar-flow air–acetylene burner.

For maximum efficiency, the gas-dispersion tubes used for aeration were bent to hook over the side of the beakers, with the fritted glass tips parallel to the bottoms of the beakers.

Reagents

Standard antimony solutions, 5, 50 and 100 μg/ml. Dissolve 0.2669 g of pure potassium antimony tartrate (dried at 105° for 1 hr) in water and dilute to 1 litre with water. Transfer a 5-ml aliquot of this 100 μg/ml stock solution to a 100-ml standard flask, and a 50-ml aliquot to another 100-ml flask. Dilute each solution to volume with water. Prepare the diluted 5 and 50 μg/ml solutions fresh as required.

Potassium iodide–ascorbic acid solution. Components 35% and 2.5% w/v, respectively. Prepare fresh as required.

Iron(III) sulphate solution (1 ml ≡ 10 mg of iron). Dissolve 25 g of ferric sulphate monohydrate in hot water containing 20 ml of 50% v/v sulphuric acid, cool and dilute to 500 ml with water.

Lanthanum chloride solution (1 ml ≡ 10 mg of lanthanum). Dissolve 12.5 g of lanthanum chloride hexahydrate in water and dilute to 500 ml with water.

Hydrochloric acid–stannous chloride–tartaric acid–thiourea solution. Prepare a sufficient volume of solution just before use, the composition being 43 ml of concentrated hydrochloric acid, 0.5 g of stannous chloride dihydrate, 2 g of tartaric acid and 0.5 g of thiourea per 100 ml.

Hydrochloric acid–tartaric acid wash solution. Dissolve 4 g of tartaric acid in water, add 430 ml of concentrated hydrochloric acid and dilute to 1 litre with water.

Potassium ethyl xanthate, 20% w/v solution. Prepare fresh as required.

Thiourea, 5% w/v solution. Prepare fresh as required.

Aqua regia. Mix 3 parts of concentrated hydrochloric acid with 1 part of concentrated nitric acid. Prepare fresh as required.

Potassium hydroxide, 10% w/v solution. Store in a plastic bottle.

Tartaric acid, 5% w/v solution.

Ammonia, 10% v/v solution.

Sulphuric acid, 50% v/v.

Hydrochloric acid, 25 and 50% v/v.

Nitric acid, 50% v/v.

Chloroform. Analytical-reagent grade.

Determination of antimony by the spectrophotometric iodide method

Calibration. Add 4 ml of 50% sulphuric acid and 1 ml of 5% tartaric acid solution to each of fifteen 25-ml standard flasks; then, from a burette, add to the first five flasks 1, 2, 3, 4 and 5 ml respectively, of standard 5-μg/ml antimony solution. Add to the next nine flasks 1, 1.5, 2, 3, 4, 6, 8, 10 and 12 ml respectively, of standard 50-μg/ml antimony solution. The last flask contains the blank. If necessary, dilute each solution to approximately 15 ml with water and cool to room temperature in a water-bath. Add 5 ml of freshly prepared 35% potassium iodide–2.5% ascorbic acid solution to each flask, dilute to volume with water and mix. Allow the solutions to stand for about 30 min to complete the complex formation, then determine the absorbance, at 331 nm, of the blank and each of the five solutions in the first series against water as the reference solution, using 40-mm cells. Determine the absorbance of the blank, the last solution in the first series, and each of the first four solutions in the second series in a similar manner, at 425 nm, using 40-mm cells. Determine that of the blank and each of the last seven solutions in the second series, at 425 nm, using 10-mm cells. Correct the absorbance value obtained for each antimony iodide solution by subtracting the corresponding blank value. Plot μg of antimony *vs.* absorbance for each series of measurements.

Copper, nickel, zinc and lead concentrates and ores. Transfer 0.05–0.5 g of sample (see Notes 1–3), containing up to 2 mg of antimony, to a 400-ml beaker. Add 25 ml of freshly prepared *aqua regia*, cover and heat gently until all or most of the sample is decomposed. Add 25 ml of 50% sulphuric acid, heat until the evolution of oxides of nitrogen ceases, then remove the cover, wash down the sides of the beaker with water, and carefully evaporate the solution to dryness. Cool, add 50 ml of 50% hydrochloric acid, cover and, if necessary, heat gently to dissolve the salts (particularly lead sulphate). Cool the resulting solution to room temperature, add 3 g of sodium metabisulphite, mix, and allow the solution to stand for ~5 min. Boil the solution (covered) for ~10 min to remove the excess of sulphur dioxide, then add 25 ml of water. Place a gas-dispersion tube in the beaker and pass air through

the solution at a fairly rapid rate for ~10 min to reoxidize any iron(II) present. Remove the tube after washing it thoroughly with water.

If necessary, add sufficient iron(III) sulphate solution to the resulting solution so that at least 50 mg of iron are present. Add 5 ml of lanthanum chloride solution and sufficient concentrated ammonia solution to precipitate iron as the hydrous oxide, then add 75 ml in excess and heat the solution to the boiling point to coagulate the precipitate. Allow it to settle and, using a short-stemmed funnel, filter the hot solution (Whatman No. 40 paper). If molybdenum and/or more than ~75 mg of copper or nickel are absent, wash the beaker twice and the paper and precipitate three times with 10% ammonia solution (Note 4). Discard the filtrate and washings.

If molybdenum and/or more than ~75 mg of copper or nickel are present, wash the beaker, the paper and precipitate once each with 10% ammonia solution. Place the original beaker under the funnel and add 25 ml of 25% hydrochloric acid to the funnel to dissolve the precipitate. Wash the paper three times with 25% hydrochloric acid added from a plastic wash-bottle, then wash down the sides of the beaker with the acid. Reprecipitate the iron and lanthanum, and filter off and wash the precipitate as described above (Note 4). Discard the filtrate. Carry a blank, with ~50 mg of iron(III) added, through the whole procedure (if some samples have high antimony content and some have low, more than one blank will be needed, see below).

Transfer the funnels containing the blank and sample precipitates to 250-ml separatory funnels, marked at 100 ml. Wash down the sides of each precipitation beaker with 25 ml of freshly prepared hydrochloric acid–stannous chloride–tartaric acid–thiourea solution (Note 5). Add each of the resulting solution to the funnel containing the corresponding precipitate and wash the beaker three times with the same acid solution added from a plastic wash-bottle. Wash the paper three times with the same acid solution, then discard the paper. Dilute each solution to the 100-ml mark with the acid each solution (Note 6), add 2 ml of concentrated hydrofluoric acid and mix thoroughly (Note 7).

Add 10 ml of chloroform and then 1 ml of freshly prepared 20% potassium ethyl xanthate solution (Note 8). Stopper and shake for 1 min. Allow several min for the layers to separate, then drain the chloroform phase into a 125-ml separatory funnel (Note 9). Extract the aqueous phase twice more, in a similar manner, with 10- and 5-ml portions of chloroform and 1 and 0.5 ml of xanthate solution, respectively then wash the aqueous phase by shaking it for ~30 sec with 3 ml of chloroform. Add 30 ml of hydrochloric–tartaric acid wash solution and 1 ml of 5% thiourea solution (Note 5) to the combined extracts, stopper and shake for 1 min. After the layers have separated, drain the chloroform phase into a 100-ml Teflon beaker (Note 10). Add 5 ml of chloroform and 0.5 ml of xanthate solution to the aqueous phase and shake for 1 min. Allow the layers to separate and drain the chloroform phase into the beaker containing the initial extract. Wash the aqueous phase by shaking it for ~30 sec with 5 ml of chloroform, then add 8 ml of 50% nitric acid to the combined extracts and heat in a hot water-bath to remove the chloroform. Add 1 ml of concentrated perchloric acid and 0.5 ml of 50% sulphuric acid, cover the beaker and heat until the evolution of oxides of nitrogen ceases. Remove the cover, wash down the sides of the beaker with water and evaporate the solution to fumes of perchloric acid. Cool to room temperature, add 5 drops of freshly prepared *aqua regia* and mix thoroughly. Wash down the sides of the beaker with water and evaporate the solution until the diameter of the drop remaining in the bottom of the beaker is 3–4 mm. Cool the beaker in a water-bath, then wash down the sides with 5 ml of 10% potassium hydroxide solution added from a pipette, and heat the solution gently for ~5 min. Cool slightly and add 1 ml of 5% tartaric acid solution and 4.5 ml (Note 11) of 50% sulphuric acid. Heat the solution gently again for ~5 min, then add ~5 ml of water and cool the resulting solution to room temperature in a water-bath (Note 12).

If the sample contains 600 μg or less of antimony, transfer the solution to a 25-ml standard flask containing 5 ml of 35% potassium iodide–2.5% ascorbic acid solution (Note 13). Treat the blank similarly. Dilute to volume with water, mix and proceed with the subsequent determination of antimony as described above (Note 14), using either 10- or 40-mm cells and a wavelength of 425 or 331 nm as required (Note 15).

If the sample contains more than 600 μg of antimony, transfer the solution to standard a flask of appropriate size (25 or 50 ml). Add sufficient additional 5% tartaric acid solution for 1 ml to be present for each 10 ml of final solution and dilute to volume with water. Transfer a 10-ml aliquot to a 25-ml standard flask and add sufficient 50% sulphuric acid for a total of 4 ml to be present. Mix and cool the resulting solution to room temperature, then proceed with the addition of potassium iodide–ascorbic acid solution and the subsequent determination of antimony as described for the calibration, using 10- or 40-mm cells as required and a wavelength of 425 nm. Treat the blank similarly.

Molybdenum ores and concentrates. Transfer up to 0.5 g of sample (see Notes 1–3) to a 400-ml beaker. Add 1.5 g of potassium chlorate, moisten with a few ml of water, cover and carefully add 20 ml of concentrated nitric acid. Heat gently until the sample is decomposed, then add 25 ml of 50% sulphuric acid and heat until the evolution of oxides of nitrogen ceases. Remove the cover, wash down the sides of the beaker with water and carefully evaporate the solution to fumes of sulphur trioxide. Cool to room temperature, add ~10 ml of water, cover and add 15 ml of freshly prepared *aqua regia*. Heat gently for 5–10 min, then remove the cover and evaporate the solution to dryness (Note 16). Proceed with the dissolution of the salts and the reduction and separation of antimony(III) by co-precipitation with hydrous ferric and lanthanum oxides as described above. Dissolve the precipitate, and reprecipitate iron and lanthanum as described, then proceed with the separation of antimony by chloroform extraction of its xanthate complex and its subsequent determination as described above, using a wavelength of 425 nm (Note 15).

Copper metal and copper- and lead-base alloys. Decompose a suitable weight of sample (0.1–0.5 g) (Notes 1 and 17), containing not more than 2 mg of antimony, and determine antimony by the method described for copper, nickel, zinc and lead concentrates.

Determination of antimony by atomic-absorption spectrophotometry

Calibration solutions. Add 2 ml of 5% tartaric acid solution, 15 ml of concentrated hydrochloric acid and 5 ml each of iron(III) sulphate and lanthanum chloride solutions to each of eight 100-ml standard flasks; then, from a burette, add to the first seven flasks 1, 3, 5, 7.5, 10, 15 and 20 ml of standard 100-μg/ml antimony solution. The last flask contains the zero calibration solution. Dilute each solution to volume with water and mix.

General procedure. Following the separation of ⩾50 μg of antimony by a single co-precipitation with hydrous ferric and lanthanum oxides as described above (Note 18), wash the beaker twice and the paper and precipitate three times with 10% ammonia solution. Discard the filtrate and washings and under the funnel, place a 100-ml standard flask containing 2 ml of 5% tartaric acid solution. Wash down the sides of the beaker with 45 ml of 25% hydrochloric acid and add the resulting solution to the funnel containing the paper and precipitate. Wash the beaker twice with ~5-ml portions of water and add the washings

to the funnel. Wash the paper three times with ~5-ml portions of 25% hydrochloric acid added from a plastic wash-bottle, then wash it twice with water. Discard the paper. Dilute the resulting solution to volume with water, mix, and measure the absorbance of the solution, at 217.6 nm, in an oxidizing air–acetylene flame. Determine the antimony content of the sample solution by relating the resulting value to those obtained concurrently for calibration solutions of slightly higher and lower antimony concentrations.

Notes

1. The use of samples containing more than ~150 mg of iron is not recommended because the mixed hydrous oxide filtration step becomes unduly slow. Low results, caused by incomplete co-precipitation of antimony, will be obtained at the 2-mg level if more than ~25 mg of either aluminium or tin, or more than ~10 mg of each, are present. Up to 50 mg of either element, when present separately, will not interfere in the co-precipitation of ≤500 μg of antimony.

2. If the sample contains an appreciable amount of silica, use a Teflon beaker and add 2–3 ml of concentrated hydrofluoric acid after the cover has been removed. Evaporate the solution to fumes of sulphur trioxide, cool to room temperature, add ~15 ml of water and heat to dissolve the salts. Transfer the solution to a glass beaker, evaporate it to dryness and proceed as described. Low results will be obtained if the excess of sulphuric acid is not removed by evaporation.

3. If the sample contains an appreciable amount of acid-insoluble material or the presence of an insoluble antimony compound is suspected, it can be decomposed by fusion as follows. Mix a suitable weight of sample, contained in a 60-ml nickel (not zirconium or iron) crucible, with 3 g of sodium peroxide and cautiously fuse the mixture over an open flame. Allow the melt to cool, then transfer the crucible to a covered 400-ml beaker (Note 2) containing 50 ml of water and 25 ml of 50% sulphuric acid. Remove the crucible immediately after the melt has dissolved and add 10 ml of 50% nitric acid to prevent (if chloride is present) the loss of antimony by volatilization as the chloride.[26] Evaporate the covered solution to ~30 ml, then remove the cover and evaporate the solution to fumes of sulphur trioxide. Cool to room temperature, add 15 ml of freshly prepared *aqua regia*, cover and heat until the evolution of oxides of nitrogen ceases. Remove the cover and evaporate the solution to dryness. Dissolve the salts in 75 ml of 50% hydrochloric acid and proceed with the reduction and a double co-precipitation of antimony as described.

4. If the subsequent xanthate extraction cannot be completed the same day, allow the precipitate to stand overnight (or longer) at this point.

5. Thiourea can be omitted if it is known that the sample contains little or no copper.

6. Unless molybdenum is present (pale yellow solution), the solution should be colourless at this point. Sufficient stannous chloride is present to reduce up to ~240 mg of iron(III).

7. To minimize the attack of hydrofluoric acid on glass, the antimony(III) xanthate extraction should be done immediately after the hydrofluoric acid has been added. Similarly, the funnel should be washed immediately after the extraction has been completed.

8. The xanthate solution should be added by pipette with use of a suction bulb (not by mouth) or by using a graduated or marked medicine dropper, and the extraction should be carried out in a fume hood. Prolonged exposure to xanthate vapour can produce an allergic reaction.

9. A reddish or purple extract indicates the presence of molybdenum.

10. Glass beakers should not be employed, because the potassium hydroxide solution subsequently used may leach antimony or lead from the glass. Teflon beakers may become partly discoloured (*i.e.*, yellow-brown or black) inside because of the subsequent use of *aqua regia* to oxidize antimony to antimony(V). Before the beakers are used again, this discolouration should be removed by heating perchloric acid to dense fumes in the covered beaker.

11. The additional 0.5 ml of 50% sulphuric acid added to the sample solution—as compared to the calibration solutions—is required to react with the potassium hydroxide.

12. Salts may crystallize from the solution on standing but these will redissolve when the solution is ultimately diluted and mixed thoroughly.

13. The presence of arsenic is signified by a deep yellow or orange colour due to iodine liberated during the reduction of arsenic(V) by potassium iodide. The iodine is subsequently reduced by ascorbic acid when the solution is mixed.

14. If the solution is slightly opalescent, filter it through a dry Whatman No. 42 filter paper before the spectrophotometric measurement.

15. If molybdenum was co-extracted as the xanthate (Note 9), absorbance measurements should be made at 425 nm, after the solution has been stood overnight to ensure complete complex formation.

16. If the residue becomes deep blue (molybdenum blue) on cooling, add ~5–10 ml of water and 2 ml of concentrated perchloric acid and evaporate the solution to dryness again.

17. If the expected antimony content is low, up to at least 1 g of sample can be used for high-purity copper metal and for copper-base alloys of low aluminium and tin content (Note 1).

18. The use of samples containing more than ~100 mg of lead is not recommended because the resultant lead chloride is not completely soluble in 15% hydrochloric acid.

RESULTS

Spectrophotometric determination of antimony by the iodide method

In initial tests, low and erratic results were usually obtained by the iodide method[25] after treatment of the antimony(III) xanthate extracts [or pure potassium antimony(III) tartrate solutions] with nitric, perchloric and sulphuric acids and evaporation of the solution to fumes of sulphur trioxide before complex formation. This was considered to be due to the formation of an insoluble basic antimony compound.[27] In subsequent work, bromide was found to interfere at low levels of antimony when antimony(III) xanthate in the extract was oxidized with bromine–carbon tetrachloride solution,[3] followed by back-extraction of antimony(V) into 10% sulphuric acid and removal of the excess of bromine by evaporation. The amount of bromide formed did not interfere at high levels of antimony (2 mg) when an aliquot of the resultant solution was taken for analysis. Hydrogen peroxide was found to be completely ineffective as an oxidant for antimony(III) xanthate.

Further tests, involving oxidation of antimony(III) xanthate with acids as described above, also usually yielded slightly low results when the solution was ultimately evaporated to dryness in Teflon beakers and

the salts were dissolved in 10% potassium hydroxide solution. The final sulphuric–tartaric acid solution obtained was also not stable on standing. Furthermore, the Teflon beakers became contaminated with μg-quantities of antimony, suggesting the presence of a compound that is insoluble in both potassium hydroxide solution and dilute sulphuric acid. Ultimately—as a result of later work involving the co-precipitation of antimony(III) with iron(III) and lanthanum—it was found that complete recovery of antimony and a stable solution are obtained if *aqua regia* is added just before the evaporation of the solution to dryness and dissolution of the salts in potassium hydroxide solution. Low results were still obtained if the potassium hydroxide treatment was omitted. A probable explanation of this anomalous behaviour of antimony is given in the discussion below.

Separation of antimony(III) by co-precipitation with hydrous ferric and lanthanum oxides

Previous investigators have recommended the separation of antimony by co-precipitation with hydrous ferric[4,5] or lanthanum oxides[8–10,14,28] but the oxidation state of antimony is usually not clearly indicated. In the present work, tests carried out to determine the required oxidation state, and also the effectiveness of iron and lanthanum individually as collectors, showed that antimony should be in the tervalent state and that lanthanum is a better collector than iron(III). Potassium antimony tartrate solutions (2000 μg of antimony) were used in these tests and potassium permanganate was employed in a hot, fairly concentrated sulphuric acid medium to oxidize antimony(III) to antimony(V) and to destroy tartrate which interferes in the co-precipitation step. In the tests involving collection of antimony(III), the resultant antimony(V) was subsequently reduced with sodium metabisulphite as described in the proposed method, and reduced iron, present in tests with iron(III), was oxidized by passing air through the solution by means of a gas-dispersion tube fitted with a fritted glass disc. Co-precipitation, at ~pH 9, with iron(III) (100 mg) was carried out as described previously for tellurium[2] and arsenic.[3] Co-precipitation, at ~pH 10, with lanthanum (100 mg) was performed as described in the proposed method. Antimony was ultimately extracted as the xanthate and the extract was treated with 5 ml of 20% bromine–carbon tetrachloride solution as described above. Interference from bromide, in the spectrophotometric iodide finish, was avoided by taking one-fifth of the final solution for the determination of antimony. Complete recovery of antimony was obtained only in the test involving the collection of antimony(III) with lanthanum (Table 1, test 1). In the tests involving collection of antimony(V), it was found necessary to dissolve the hydrous oxide precipitate with 5*M* hydrochloric acid containing stannous chloride so that antimony(V) was immediately reduced to antimony(III) (for the xanthate extraction) during the dissolution step. Much lower results were obtained if 5*M* hydrochloric acid alone was used and antimony and iron were subsequently reduced with stannous chloride. No doubt, this is due to the formation of unreactive antimony(V) hydrolysis compounds in the hydrochloric acid medium.[21,22]

Subsequent work involving collection of antimony(III) with lanthanum (100 mg) (see Table 1), followed by xanthate extraction and the iodide finish, invariably yielded low results when pure antimony(III) solutions were treated with nitric acid or nitric and perchloric acids. However, complete recovery of antimony was obtained when an atomic-absorption finish was used after dissolution of the lanthanum precipitate. This indicated that the low results obtained in the xanthate–iodide scheme were due to incomplete formation of antimony(III) xanthate. The results of tests 4 and 5 in Table 1 suggested that the pretreatment of the solutions with nitric acid was, in some way, responsible for this behaviour. The fact that complete recovery of antimony was obtained in test 3, in which it was present as antimony(V) before the addition of nitric acid, suggested that the use of nitric acid probably results in the formation of an unreactive oxidized species that is not reduced by either sodium metabisulphite or hydrazine sulphate, or with stannous chloride during the dissolution of the lanthanum precipitate. The formation, during oxidation of antimony with nitric acid or nitric and sulphuric acids, of an unreactive species which is not easily oxidized has been described by Maren.[29] However, although Maren found that this species, referred to as antimony(IV), can be oxidized with perchloric acid and easily reduced with sulphite, these properties do not agree with those found in the present work (see tests 4 and 5, Table 1).

On the basis of these findings, it was considered that complete recovery of antimony by use of the xanthate–iodide scheme could only be obtained if it was completely oxidized to antimony(V) during the decomposition procedure. In this state, it is readily reduced to antimony(III). The results of subsequent tests, in which a certified, high-antimony, reference ore, CD-1,[30] was decomposed (in a zirconium crucible) by an oxidizing fusion with sodium peroxide, are given in Table 2. In these tests, hydrazine sulphate was used as reductant (see Table 1, test 3 for conditions) and iron(II) was reoxidized as described in the proposed method. Both iron(III) and lanthanum (50 mg of each) were used for co-precipitation because this mixture produces a more readily filterable precipitate than lanthanum alone. The use of nitric acid after fusion was tested because it is required in the presence of chloride to prevent loss of antimony by volatilization as the chloride[26] during subsequent evaporation of the solution. Tests 1–4 show that antimony is not completely oxidized to antimony(V) during fusion with sodium peroxide unless an auxiliary oxidizing compound such as potassium nitrate (see

Table 1. Effect of preliminary acid treatment on the determination of antimony by the iodide method after lanthanum collection and xanthate extraction

Test	Preliminary treatment of pure Sb(III) solutions*	Method of reduction used	Sb found, μg
1	$KMnO_4$ oxidation in H_2SO_4 medium and evaporation to dryness	$Na_2S_2O_5$ (3 g) in 6*M* HCl	2005
2	$KMnO_4$ oxidation in H_2SO_4 medium	$N_2H_4.H_2SO_4$ (1 g) and evaporation to dryness + salts dissolved in 6*M* HCl	1988
3	$KMnO_4$ oxidation in H_2SO_4 medium + HNO_3 and evaporation to fumes of SO_3	As in test 2	2012,1992
4	HNO_3 + H_2SO_4 and evaporation to fumes of SO_3	As in test 2	1969
5	HNO_3 + $HClO_4$ + H_2SO_4 and evaporation to dryness	As in test 1	1869

* Sb(III) taken, 2000 μg.
† Required to destroy the excess of reductant.

tests 6 and 7) is present. This also suggests that an unreactive species is formed during fusion with sodium peroxide, and that it is not reduced with hydrazine sulphate or sodium metabisulphite (test 8), and not oxidized with potassium permanganate (test 3), or with potassium chlorate (test 4) unless nitric acid is absent (test 5). Although it was ultimately found that zirconium, derived from the crucible, can interfere in the co-precipitation of antimony with lanthanum, the results of test 8 in which nickel crucibles were used, confirm these conclusions (*cf.* test 14).

A mixture of sodium peroxide and potassium nitrate cannot be used for the decomposition of sulphide-containing materials because of the violence of the reaction. Consequently, the effectiveness of various oxidizing agents was tested in conjunction with the decomposition of CD-1 with acids. The results of these tests, given in Table 2, ultimately showed that a mixture of potassium chlorate and perchloric acid (test 12) is effective in the absence of nitric acid, but that *aqua regia* (test 13) is a superior oxidizing agent for antimony. It can be used after fusion with sodium peroxide (test 14) and, because of the nitric acid content, antimony is not lost as the volatile chloride. It was also found that the use of *aqua regia* eliminated the problem of low and erratic results which was encountered in initial work involving the treatment of the xanthate extracts with acids.

Preliminary experiments, in which synthetic concentrates [2000 μg of antimony(III) added] were

Table 2. Effect of method of decomposition on the determination of antimony in CD-1* by the iodide method after iron–lanthanum collection and xanthate extraction

Test	Method of decomposition used	Sb found, %
1	Na_2O_2 fusion (Zr crucible)—melt dissolved in dilute H_2SO_4—HNO_3 + HF added and evaporation to fumes of SO_3	3.45
2	As for test 1 without the addition of HNO_3	3.35
3	Na_2O_2 fusion (Zr crucible)—melt dissolved in water—boiled to remove peroxides—H_2SO_4 + $KMnO_4$ + HNO_3 + HF added and evaporation to fumes of SO_3	3.41
4	As for test 1 except $KClO_3$ added just before evaporation to fumes of SO_3	3.38
5	As for test 4 without the addition of HNO_3	3.58
6	Na_2O_2 + KNO_3§ fusion (Zr crucible)—melt dissolved in dilute H_2SO_4—HNO_3 + HF added and evaporation to fumes of SO_3	3.59
7	As for test 6 without the addition of HNO_3	3.62
8	Na_2O_2 fusion (Ni crucible)—as for test 1 except solution evaporated to dryness†	3.42‖
9	H_2SO_4 + HF + $HClO_4$ and evaporation to fumes of SO_3	3.47
10	H_2SO_4 + HNO_3 + HF + $KClO_3$ and evaporation to fumes of SO_3	3.41
11	As for test 9 without the addition of HNO_3	3.49
12	H_2SO_4 + HF + $HClO_4$ + $KClO_3$ and evaporation to fumes of SO_3	3.58
13	*Aqua regia* + H_2SO_4 + HF and evaporation to fumes of SO_3	3.57
14	Na_2O_2 fusion (Ni crucible)—as for test 1 except *aqua regia* added after evaporation to fumes of SO_3 followed by evaporation to dryness†	3.58¶

* 50 mg samples taken; certified value 3.57% Sb.[30]
§ 200 mg added.
† Antimony reduced with sodium metabisulphite in 50% hydrochloric acid.
‖ Mean of 4 values, viz. 3.38, 3.46, 3.49 and 3.36%.
¶ Mean of 2 values, viz. 3.55 and 3.61%.

decomposed with *aqua regia*, and then, except for the use of hydrazine sulphate as reductant, were treated as described in the proposed spectrophotometric method, gave recoveries of 90–95% for copper and molybdenum concentrates, and complete recovery for lead and zinc concentrates. It was found that this was due to the use of hydrazine sulphate as reductant. Copper and molybdenum are partially reduced with this reagent and cause co-oxidation of antimony(III) during the air-oxidation step.[31,32] Complete recovery was obtained for copper and molybdenum concentrates when antimony was reduced with sodium metabisulphite in ~50% hydrochloric acid.[32] Under these conditions, minimal reduction of copper and molybdenum occurs.

Separation of antimony by extraction of its ethyl xanthate complex

Previous work by the author[1] showed that antimony(III) xanthate can be quantitatively extracted into chloroform from 0.1–5*M* hydrochloric acid, and that iron(II), and lead, which forms an insoluble iodide,[25] are not co-extracted from 5*M* acid media. Furthermore, although thallium(III), which also forms an insoluble coloured iodide, is appreciably extracted from 5*M* hydrochloric acid, thallium(I) is not extracted from ≥0.5*M* acid media.[1] Subsequent work by the author resulted in the development of methods for tellurium[2] and arsenic[3] in ore concentrates. These are based on the separation of tellurium and arsenic from iron and lead by xanthate extraction from ≥11*M* hydrochloric acid media, after their preliminary separation from copper, zinc, nickel and molybdenum matrices by co-precipitation with iron(III). Antimony can also be separated from these elements by similar co-precipitation techniques.[4,5,8–10,14,28] Consequently, the development of a similar method for small amounts of antimony, based on xanthate extraction from a 5*M* hydrochloric acid medium in the presence of a suitable reductant for iron and thallium, was investigated.

In a recent method for determining bismuth,[24] also based on a xanthate–iodide scheme, interference from small amounts of lead that are co-extracted as the xanthate is eliminated by washing the chloroform extract with a solution of the same hydrochloric acid concentration as the medium used for extraction. In the present work, similar tests showed that washing the xanthate extract with 5*M* hydrochloric acid effectively removes bismuth, which is partly extracted from 5*M* acid and would interfere in the determination of antimony as the iodide.[25] No interference was observed in tests involving 15 μg of antimony(III) and 5 mg of bismuth when absorbance measurements were made at 331 nm. Up to 10 mg of bismuth can be present during the extraction step without producing significant error. Similarly, after the washing step, no interference was observed at 331 nm when 300 mg of lead were present during the extraction step. In these tests, any antimony that entered the wash solution was recovered by adding xanthate solution and re-extracting the antimony. It was found that up to at least 2 mg of antimony(III) as the xanthate can be quantitatively extracted into chloroform in three successive extractions. In tests with iron(III) and thallium(III), slightly high results were obtained at 331 nm when stannous chloride was used as a reductant for both elements. This was due to the co-extraction, as the xanthate, of a small amount of tin that was not completely removed by the washing step. This was obviated by complexing tin with hydrofluoric acid before the extraction of antimony(III) xanthate.

Effect of diverse ions

Selenium(IV), tellurium(IV), arsenic(III) and palladium(II) are completely extracted into chloroform as xanthate complexes from 5*M* hydrochloric acid, and copper(II), platinum(IV), gold(III), and molybdenum(VI) are partly extracted. Selenium and tellurium will not interfere in the proposed iodide method because they are reduced to the elemental state with stannous chloride before the extraction of antimony(III) xanthate. Palladium, platinum and gold are almost completely separated from antimony by the co-precipitation step. Up to at least 1 mg of each will not interfere after a single ammonia separation. Up to at least 10 mg of arsenic will not interfere, either in the extraction of up to 2 mg of antimony or in the determination of small amounts at either 331 or 425 nm. The co-extraction of copper that is retained in the mixed hydrous oxide precipitate can be largely prevented or inhibited by complexing it with thiourea.[1] Molybdenum, which is also retained in the precipitate and subsequently co-extracted as the xanthate, causes high results for small amounts of antimony at 331 nm but not at 425 nm. It also slightly inhibits complex formation when ~100 μg or more of antimony are present, but this effect can be eliminated or minimized by allowing the solution to stand for ~24 hr before measuring the absorbance.

Up to at least 50 mg of manganese will not interfere in either the proposed iodide or atomic-absorption methods. However, the same amount of vanadium causes low results by both methods, probably because it is reduced to vanadium(IV) during the initial reduction step. This is probably partly oxidized during the air-oxidation step and causes some co-oxidation of antimony(III). Large amounts of chromium (50 mg) interfere because an insoluble compound is formed during the co-precipitation step. Small amounts of these elements will not interfere.

It has been reported that other elements that form hydrous oxides, notably iron and aluminium, do not interfere in the co-precipitation of antimony with lanthanum. However, tests involving an atomic-absorption finish, after dissolution of the iron–lanthanum precipitate, showed that large amounts (50 mg) of aluminium, zirconium and tin interfere at the 2-mg level when 50 mg of lanthanum are used. This is probably

because they preferentially form similar compounds with lanthanum or partly soluble compounds with antimony. Up to ~25 mg of each, when present separately, or ~10 mg each of aluminium and tin, will not interfere in the co-precipitation of up to 2 mg of antimony; 50 mg of either aluminium or tin will not affect the co-precipitation of ≤500 μg. Larger amounts can be tolerated if more lanthanum is used but this results in a bulkier precipitate that takes longer to filter. Furthermore, when the precipitate contains 50 mg or more of aluminium, the resultant solution passes very slowly through the filter paper. In the absence of these and other hydrous oxides, 50 mg of lanthanum will be sufficient for the co-precipitation of up to at least 10 mg of antimony. Zirconium and iron crucibles are not recommended for fusion purposes because zirconium interferes and because too much iron would be introduced into the resultant sample solution.

Tests, which were carried out to determine the effects of iron and other co-precipitated elements on the determination of 5 μg/ml of antimony by atomic-absorption spectrophotometry, showed that up to at least 500 μg/ml of copper, tin, aluminium, nickel, molybdenum, manganese and zinc, 1000 μg/ml of lead and sodium, 1500 μg/ml of iron, and 200 μg/ml of arsenic will not interfere. More than ~1000 μg/ml of lead will cause slightly high results and may result in the precipitation of lead chloride in the solution.

Applications

The proposed spectrophotometric method was applied to the analysis of a series of four synthetic concentrates (ground to 200-mesh) in which antimony, added as antimony(III), was varied from 0.0005 to 1%. Because a lead sulphide concentrate of low antimony content could not be obtained, synthetic mixtures of lead sulphate and other elements usually found in commercial concentrates were used. Both of the proposed methods were applied to a variety of certified reference materials, and several commercial-purity copper rods[33] were analysed by the iodide method. The results of these analyses are given in Tables 3 and 4.

DISCUSSION

Table 3 shows that the results obtained for the synthetic concentrates by the spectrophotometric iodide method agree favourably with the calculated values. Those obtained for the synthetic nickel concentrate are also in reasonably good agreement with the calculated values, although it was found that the concentrate was not homogeneous with respect to antimony; the mean value (reported in the footnote to Table 3) of seven results was used to calculate the total amount present. The results (Table 4) obtained for CD-1, CPB-1 and CZN-1 by the spectrophotometric iodide method, after sample decomposition both by fusion and with acids, are in excellent agreement with those obtained by the atomic-absorption method. The results by both methods are also in good agreement with the corresponding recommended mean values. The results for the National Bureau of Standards and British Chemical Standards non-ferrous alloys by both methods are in good agreement and, in most instances, agree well with the certified values. Those obtained for the copper rods by the iodide method agree with the recommended values.

This investigation has shown (Tables 1 and 2) that the nature of the decomposition method employed, before the separations of antimony by co-precipitation with lanthanum followed by xanthate extraction, can cause a significant difference in the results obtained for antimony. This is because of the formation of an unreactive species when the decomposition procedure initially involves the use of nitric and/or perchloric acids or fusion with sodium peroxide. Although tests involving an atomic-absorption finish have shown that this species is completely co-precipitated with lanthanum, apparently it is not reduced with tin(II) during the subsequent dissolution of the precipitate with hydrochloric acid containing stannous chloride. In early work, this apparent and variable loss of antimony during acid digestions in the presence of oxidizing acids such as those listed above or hydrogen peroxide[34,35] was attributed to volatilization of antimony.[34] Later, Maren[29] showed that it was caused by partial oxidation to an unreactive state, which he called antimony(IV) because it was known that nitric acid oxidation of antimony results in partial formation of a tetroxide (Sb_2O_4). This has a definite composition and is still used as a weighing form for the gravimetric determination of antimony.[5] However, titrimetric[36] and recent Mössbauer studies[37] have shown that the tetroxide, which is presumably the dehydrated form of the unreactive compound mentioned above, is a compound containing antimony(III) and antimony(V) in a 1:1 ratio (*i.e.*, $Sb_4O_8 = Sb_2O_3 + Sb_2O_5$). Maren[29] found that this compound, hereafter referred to as antimony (III + V), is not readily oxidized [with cerium(IV)] to antimony(V), which is required for the formation of the Rhodamine B complex, unless it is first reduced to antimony(III) with sulphite. However, he found that it can be oxidized with perchloric acid. In the present work, it was found that the antimony(III + V) species is not readily oxidized with perchloric acid, potassium permanganate or potassium chlorate, but that it is completely oxidized to antimony(V) with *aqua regia*. It was also found, contrary to Maren's findings, that it is not reduced by either sulphite or hydrazine sulphate. However, tests with reference ore CD-1 involving direct formation of the iodide complex, after decomposition under conditions that favour the formation of the unreactive species, showed that this species is reduced by potassium iodide.

Table 3. Recovery of antimony from synthetic concentrate samples

Matrix and nominal composition, %	Total Sb present, %	Sb found, % Iodide method
Cu concentrate (24.7 Cu, 30.7 Fe, 35.6 S, 3.2 Zn, 1.2 Si)	0.0005_0	0.0006_6
	0.0010_0	0.0011_5
	0.0050_0	0.0052_0
	0.0100	0.010_0
	0.0500	0.050_0
	0.1000	0.100_4
	0.500	0.49_9
	1.000	1.01_1
Mo concentrate (95.9 MoS_2)	0.0019_0	0.0021_0
	0.0024_0	0.0022_0
	0.0064_0	0.0062_0
	0.0114	0.010_9
	0.0514	0.050_0
	0.1014	0.099_4
	0.501	0.49_2
	1.001	0.99_6
Ni concentrate (33.3 Ni, 30.2 Fe, 32.1 S, 4.5 Cu, 0.2 As, 0.02 Bi)	0.0023_4	0.0027_2
	0.0028_4	0.0034_4
	0.0068_4	0.0067_0
	0.0118	0.011_9
	0.0518	0.050_8
	0.1018	0.100_0
	0.502	0.49_5
	1.002	0.99_6
Zn concentrate (50.6 Zn, 33.5 S, 10.1 Fe)	0.0009_6	0.0010_2
	0.0014_6	0.0013_4
	0.0054_6	0.0054_0
	0.0105	0.010_9
	0.0505	0.049_5
	0.1005	0.098_5
	0.501	0.50_4
	1.001	0.98_4
Pb concentrate (68 Pb, 10 Fe, 0.2 Bi, 0.4 As, 2 Cu)	0.0005_7	0.0006_2
	0.0010_7	0.0010_7
	0.0050_7	0.0052_0
	0.0101	0.010_1
	0.0501	0.051_0
	0.1001	0.100_0
	0.500	0.50_0
	1.000	0.99_8

Duplicate determinations of antimony in the Cu, Mo, Zn and Pb concentrates by the proposed iodide method gave none detected and none detected, 0.0014_0 and 0.0014_0, 0.0005_1 and 0.0004_0, and 0.0001_3% and none detected, respectively. Seven determinations of antimony in the nickel concentrate—ranging from 0.0011_8 to 0.0027_9%—gave a mean value of 0.0018_4%.

On the basis of the findings above regarding the inertness of the antimony(III + V) species to both oxidation and reduction, it is emphasized that decomposition procedures that result in the formation of this compound, or the use of oxidants or reductants that do not completely convert it into the desired oxidation state, may ultimately cause low results for antimony if the methods used involve complexation reactions for separation purposes and/or for spectrophotometric finishes. Similarly, low results may also be obtained by such methods when antimony(V) is present in hydrochloric acid or sulphuric acid–chloride media because of the rapid formation of hydrolysed species.[21–23,38] Neither the formation of the antimony(III + V) species nor the hydrolysis products of antimony(V) in acidic chloride media affect the determination of antimony by atomic-absorption spectrophotometry. This suggests that these species are present in a true or colloidal solution.[38]

It is considered that the low and erratic results usually obtained in initial tests involving the treatment of the xanthate extract with nitric, perchloric and sulphuric acids were due to the formation of both basic antimony(V) and antimony(III + V) compounds [or to basic antimony(V) compounds alone if *aqua regia* was added before evaporation to fumes of sulphur trioxide] that are not completely soluble in dilute sulphuric acid.[27] Although antimony(V) compounds are appreciably soluble in potassium hydroxide solution, probably the antimony(III + V) compound is not, because it has been reported that the tetroxide is not very soluble in sodium hydroxide.[36] This would explain why low results were often

Table 4. Determimation of antimony in reference ores and concentrates, CD-1, CPB-1 and CZN-1, in N.B.S. and B.C.S. non-ferrous alloys and in commercial-purity copper rods[33]

Sample	Nominal composition, %	Certified value and range, % Sb	Sb found, %	
			Iodide method	Atomic-absorption method
CD-1-Antimony ore	32.9 Si, 0.7 As, 5.5 Al, 1.4 Ca, 2.8 Fe	3.57 (3.53–3.60)*	3.57†, 3.58‡	3.58†, 3.62‡
CPB-1-Lead concentrate	64.6 Pb, 4.4 Zn, 8.5 Fe, 17.8 S, 0.3 Cu, 0.3 Si, 0.6 Ca, 0.06 Ag, 0.06 As, 0.02 Bi, 0.2 Al	0.36 (0.34–0.39)*	0.370‖, 0.371‡	0.367
CZN-1-Zinc concentrate	44.5 Zn, 7.4 Pb, 11.0 Fe, 30.2 S, 0.1 Cu, 0.5 Si, 0.2 Mn, 0.03 As, 0.1 Al	0.052 (0.050–0.055)*	0.054‖, 0.055‡	0.054
NBS-C1101 Cartridge brass B	69.5 Cu, 30.3 Zn	0.012	0.012	0.011, 0.011
NBS-C1102 Cartridge brass C	72.9 Cu, 27.1 Zn	0.005	0.0049	0.0036
NBS-C1120 Aluminum brass C	80.1 Cu, 18.1 Zn, 1.5 Al, 0.09 As	0.100¶	0.092, 0.091	0.095
NBS-62b Manganese bronze	57.4 Cu, 38.0 Zn, 1.3 Mn, 1.0 Al, 1.0 Sn, 0.8 Fe	0.005a (0.005–<0.01)	0.011, 0.011	0.009
NBS-63c Phosphor bronze bearing metal	80.5 Cu, 9.4 Pb, 9.0 Sn, 0.2 P, 0.02 As	0.52 (0.50–0.54)	0.512, 0.510	0.513
NBS-127A Solder	30.0 Sn, ~70 Pb, 0.13 As, 0.04 Bi	0.79 (0.78–0.80)	0.791	0.797, 0.792b
BCS-183/1 Bronze	84.8 Cu, 5.0 Sn, 5.2 Zn, 3.5 Pb, 0.5 P, 0.14 As	0.24 (0.23–0.24)	0.234, 0.239	0.240
BCS-183/3 Leaded gunmetal	84.5 Cu, 6.7 Sn, 3.3 Zn, 3.4 Pb, 1.5 Ni, 0.15 As	0.25 (0.24–0.27)	0.252, 0.254	0.261
BCS-207/2 Gunmetal	87.3 Cu, 9.7 Sn, 1.6 Zn, 0.7 Pb, 0.07 As, 0.04 Bi	0.10 (0.093–0.11)	0.093, 0.094	0.098
BCS-207 Bronze "C"	86.8 Cu, 9.8 Sn, 2.5 Zn, 0.05 As	0.04 (0.03–0.05)	0.045, 0.044	0.043
SSC-2-Copper rod	~100 Cu	0.0006	0.0005, 0.0005	—
SSC-4-Copper rod	~100 Cu	0.0011	0.0013, 0.0013	—

* 95% confidence limits of the recommended mean value.
† Mean of 2 values after sample decomposition with acids.
‡ Mean of 2 values after sample decomposition by fusion (described in Note 3).
‖ Mean of 10 values after sample decomposition with acids.
¶ N.B.S. provisional result.
a Certified value based on the 2 results shown in brackets.
b Direct determination of antimony, *i.e.*, without co-precipitation.

obtained, and why the Teflon beakers used became contaminated with small amounts of antimony, when these acid mixtures were evaporated to dryness and the salts were dissolved in potassium hydroxide solution before the formation of the iodide complex. This view is supported by the fact that complete recovery of antimony is obtained when *aqua regia* is added after the removal of nitric acid by evaporation as described in the proposed method. Under these conditions, the antimony(III + V) compound is completely oxidized to antimony(V) which, on evaporation of the resultant solution to dryness, forms salts that are completely soluble in potassium hydroxide solution.

Although Maren[29] suggests that decomposition with sulphuric acid alone produces only antimony(III), this was not confirmed later[17] or in the present work. Low results were obtained by the iodide method, in tests with solutions prepared by dissolving antimony metal in hot concentrated sulphuric acid, when antimony was subsequently extracted as the xanthate in the absence of stannous chloride as reductant. This shows that some oxidized antimony was present, as otherwise the extraction would have been quantitative. Complete extraction was obtained in the presence of stannous chloride.

In the present work, it is recommended that any iron that is reduced to iron(II) during the initial reduction of antimony should be reoxidized to iron(III), before the co-precipitation step, by passing air through the solution. Antimony(III) is not oxidized to either antimony(III + V) or antimony(V) under these conditions. Reoxidation of the reduced iron by adding nitric acid and boiling the solution before the co-precipitation of antimony(III) with hydrous ferric oxide has been recommended.[5] However, in initial work it was found that this often produces low and erratic results for antimony. It is reasonable to assume that some oxidation of antimony(III) to both antimony(III + V) and antimony(V) will occur under these conditions.

From the results obtained in the present investigation, it is recommended that antimony should be present as antimony(III) before its co-precipitation with a mixture of iron(III) and lanthanum. However, trace amounts (μg-quantities), present as antimony(V), can probably be separated in a single co-precipitation with iron and lanthanum without causing significant error in the result. Large amounts of antimony(V) should not be separated by this method because the results obtained will be low. Four tests with CD-1 (100 mg), involving single co-precipitations of antimony(V) and its subsequent determination by atomic-absorption spectrophotometry, yielded results ranging from 3.33 to 3.45%. Lower results are obtained if a double precipitation is performed.

The proposed methods are suitable for samples containing ~0.0001% or more of antimony. The atomic-absorption method, which involves only a single co-precipitation step, is recommended for samples containing ~0.01% or more because it is considerably simpler and much faster than the spectrophotometric iodide method. The accuracy with which antimony can be determined at the 1-μg/g level depends primarily on the antimony content of the concentrated ammonia solution used for precipitation and neutralization purposes. This was found to vary considerably from bottle to bottle. In this work, the reagent blank obtained after single and double ammonia separations contained ~2–3 and 3–5 μg of antimony, respectively.

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SIMULTANEOUS DETERMINATION OF SO_2, NO AND NO_2 IN AIR BY DIFFERENTIAL PULSE POLAROGRAPHY

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Summary—The method of Garber and Wilson for SO_2 determination has been tested on real samples of air. The results demonstrate the possibility of simultaneous determination of SO_2, NO and NO_2 in the sample. Detection limits as low as 7 $\mu l/m^3$ for SO_2 and about 50 $\mu l/m^3$ for nitric oxides can be reached.

Sulphur dioxide is considered to be one of the five main pollutants in the atmospheric environment, the others being carbon monoxide, nitrogen oxides (NO_x), hydrocarbons and particulate matter. Sulphur dioxide is dangerous at levels as low as 30 $\mu l/m^3$ for vegetation and 0.1–0.2 ml/m^3 for men.[1] Nitrogen oxides (NO_x) are harmful because they are responsible for the production, through a complex chain of reactions, of some dangerous substances such as ozone, free radicals, peroxyacyl nitrates *etc.*, which make up the well-known photochemical smog.

Many methods have been proposed for the analytical determination of sulphur dioxide, including spectrophotometry,[2] fluorescence,[3] chromatography,[4] chemiluminescence,[5] infrared,[6] microwave[7] and mass spectroscopy.[8] Several electroanalytical methods have also been suggested[9–16] but they generally lack selectivity or sensitivity. On the other hand, the spectroscopic methods require expensive instrumentation.

There is also a large choice of methods for NO_x, starting with the classical Saltzman method.[17] The subject has recently been extensively reviewed.[18]

A very promising method has recently been proposed by Garber and Wilson[19] for sulphur dioxide determination, based on differential pulse polarography (dpp) in dimethylsulphoxide (DMSO). We thought it useful to test this method thoroughly. Our results differ in some respects from those of Garber and Wilson, especially with regard to interferences. We find, for instance that NO and NO_2 not only do not interfere in the SO_2 determination but they can be determined simultaneously with SO_2. We have also compared this method with the classical ones for analysis of samples of air.

EXPERIMENTAL

Reagents

Dimethylsulphoxide (Carlo Erba R.P.E.) was refluxed over calcium hydride overnight and then distilled at 4 mmHg and 52°. The fraction distilled was passed through molecular sieves and collected under a nitrogen atmosphere. Lithium chloride was recrystallized from ethanol and dried *in vacuo*. SO_2, NO_2, NO, H_2S (Matheson) were directly bubbled from the cylinder into DMSO. In this way relatively concentrated solutions were obtained, that were titrated with ceric ammonium nitrate. Although this reagent is reported not to oxidize DMSO[20,21] we have found that cerium(IV) solutions in DMSO are not stable. However, reduction of the cerium(IV) is very slow and aqueous cerium(IV) solutions can be used for titration of reducing agents in DMSO. We have found that reproducible and accurate results can be obtained with nitrite and sulphite. It is interesting to note that in DMSO, oxidation of sulphite involves only one electron per ion, whereas in aqueous medium it involves ten electrons for seven sulphite ions.[22]

Apparatus

A PAR 174 A polarograph with a mercury drop timer was employed. Differential pulse polarograms were obtained under the following conditions: scan-rate 2 mV/sec, modulation amplitude 50 mV, drop-time 2 sec. The reference electrode was calomel in 0.1*M* lithium chloride in DMSO. Its performance is discussed in the following section.

RESULTS AND DISCUSSION

SO_2 determination

The d.c. polarograms of sulphur dioxide in DMSO show a wave at $E_{1/2} = -875$ mV *vs.* our electrode, and log $(i_d - i)/i$ plotted *vs.* E gives a slope of 57.5 mV. This is not completely in accordance with Garber and Wilson,[19] who found a slope of 90 mV.

According to Garber and Wilson, in the dpp mode SO_2 in DMSO produces a peak between -700 and -800 mV. Employing the reference electrode (Ag/AgCl/0.1*M* LiCl in DMSO) they used in their work, we have recorded peaks at potentials ranging between -769 and -888 mV. In our opinion this is due to a lack of stability in the reference electrode potential. The unsuitability of the Ag/AgCl electrode for use in DMSO is known.[23–28] The reason for it is the formation of the relatively easily soluble $AgCl_2^-$ complex in the presence of excess of chloride ions. In contrast, our calomel electrode showed a maximum variation in potential of only 1.5 mV over several months, in spite of the claim[29,30] that it is

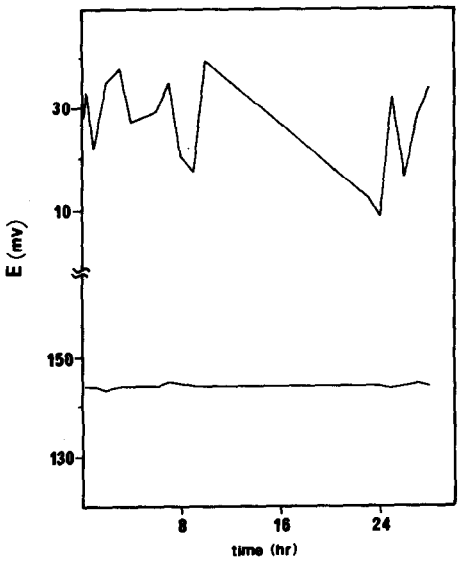

Fig. 1. Stability of DMSO calomel electrode and Ag/AgCl electrode, measured *vs.* S.C.E.

unstable. Figure 1 demonstrates the stability of the Ag/AgCl and calomel electrodes over a whole day. In fact, the dpp polarograms for sulphur dioxide show a peak at a potential which, measured with respect to the calomel electrode, varies by no more than 5 mV (which is the experimental error). This is particularly important in the case of the low sulphur dioxide concentrations because oxygen gives a peak only about 50 mV less cathodic than that for sulphur dioxide (at −860 mV *vs.* our reference electrode) which could be erroneously interpreted as the sulphur dioxide peak if the potential were not well defined. The calibration curve obtained for sulphur dioxide had a slope essentially the same as that found by Garber and Wilson (14.3 *vs.* 13 nA μmole^{-1}).

Using the usual statistical methods[31,32] we have calculated the detection limit (d.l.) defined by the relationship

$$\text{d.l.} = S_0 \sqrt{\frac{N-2}{N-1}} \frac{t_p}{b}$$

where

$$S_0 = \{[\Sigma(I - I_{calc})^2]/(N\text{-}2)\}^{1/2},$$

N is the number of experimental points, b the slope of the straight line and t_p the value of Student's t at the chosen confidence limit. For our calibration curve, d.l. is 0.18 μM, *i.e.*, 12 μg/l. in DMSO. This corresponds to a detectable quantity of about 7 μl/m^3 (or 20 μg/m^3) in air by sampling for 30 min at a flux of 1 l./min.

NO and NO_2

Figure 2 shows a polarogram of sulphur dioxide in the presence of nitric oxide and nitrogen dioxide. No effect on the sulphur dioxide peak-height can be detected, but three additional peaks appear at potentials of −1298, −1444, and −1800 mV. The polarogram remains unchanged for several hours. No variation in the peak-height is observed if nitrogen is bubbled through the solution.

Separate dpp voltammograms were obtained for various concentrations of nitric oxide and nitrogen dioxide. Nitric oxide gives two peaks at −1444 and −1800 mV, and nitrogen dioxide shows three peaks at −1298, −1444 and −1800 mV.

Polarographic measurements (d.c.) on the nitrogen oxides were performed by Gritzner, Gutmann and Schober,[33] who found that nitrogen dioxide gave waves at −1060 and −1530 mV *vs.* S.C.E.

Figure 3 shows the calibration curves for nitric oxide and nitrogen dioxide, for the three potentials −1298, −1444 and −1800 mV. Calibration at −1298 mV is necessary for nitric oxide because the NO peak at −1444 mV is very broad and overlaps the nitrogen dioxide peaks at −1298.

When both nitrogen oxides are present, the currents obey the relationships

$$i_{1298} = 3.87\, C_{NO_2} + 0.52\, C_{NO} \quad (1)$$

$$i_{1444} = 2.33\, C_{NO_2} + 2.54\, C_{NO} \quad (2)$$

$$i_{1800} = 3.13\, C_{NO_2} + 3.33\, C_{NO} \quad (3)$$

where i is in nA and C in μmole/l.

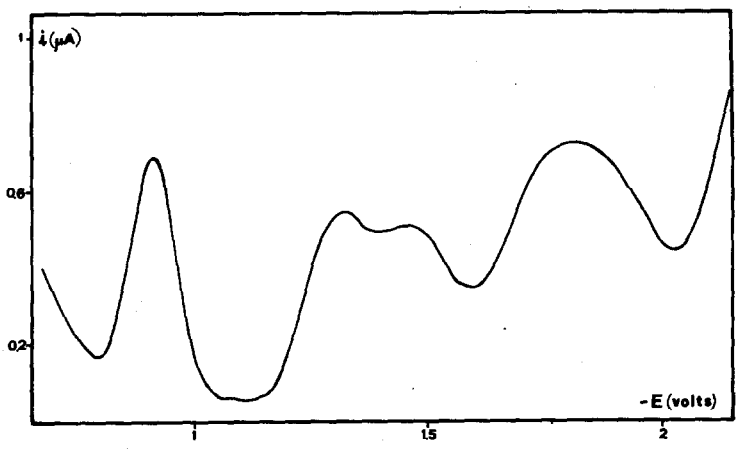

Fig. 2. Voltammogram (dpp) of SO_2 in the presence of NO and NO_2. $C_{SO_2} = 4.4 \times 10^{-5} M$, $C_{NO} = 0.98 \times 10^{-4} M$, $C_{NO_2} = 1.05 \times 10^{-4} M$.

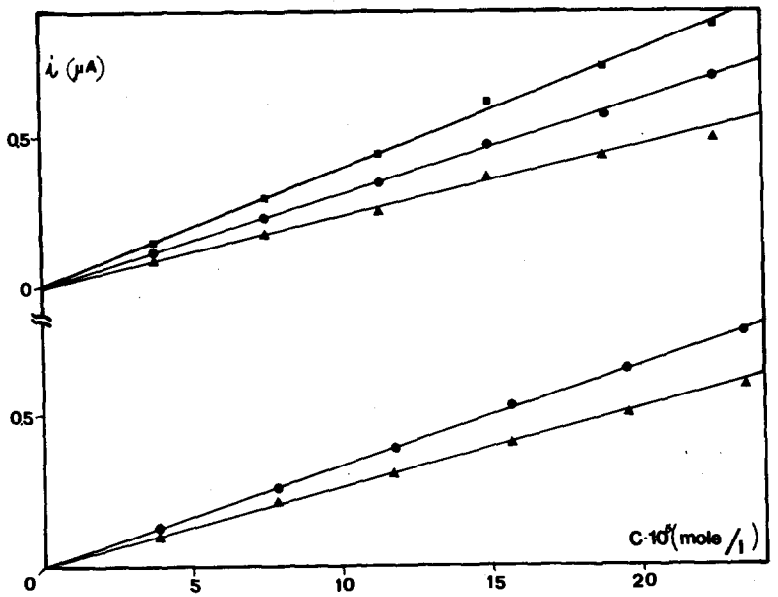

Fig. 3. Calibration plot of NO_2 (upper three lines) and of NO (lower two lines).

C_{NO} and C_{NO_2} can be calculated from (1) and (2), and the current at −1800 mV is nearly proportional to the sum of the concentrations. Table 1 shows the results for analysis of various mixtures of nitrogen oxides in DMSO.

Interferences

Carbon monoxide and dioxide do not interfere at concentrations up to saturation (115 and 6300 ppm respectively). Contrary to Garber and Wilson we found that hydrogen sulphide causes deformation of the sulphur dioxide peak when present at about the same concentration. Figure 4 shows the dpp polarogram of $3.6 \times 10^{-4}M$ sulphur dioxide at various concentrations of hydrogen sulphide. The shape of the sulphur dioxide peak is restored by deaeration of the solution.

Table 1.

Added, μmole/l.			Found, μmole/l.		
C_{NO_2}	C_{NO}	$C_{NO} + C_{NO_2}$	C_{NO_2}	C_{NO}	$C_{NO} + C_{NO_2}$
183	18	201	170	26	196
226	64	290	224	70	294
116	72	188	122	64	101
75	23	98	82	19	186

Water causes an anodic shift of the sulphur dioxide peak but, up to concentrations of 12% w/w, has no effect on the peak height.

Analysis of air

To test the validity of the method we analysed air sampled near sites of fuel combustion.

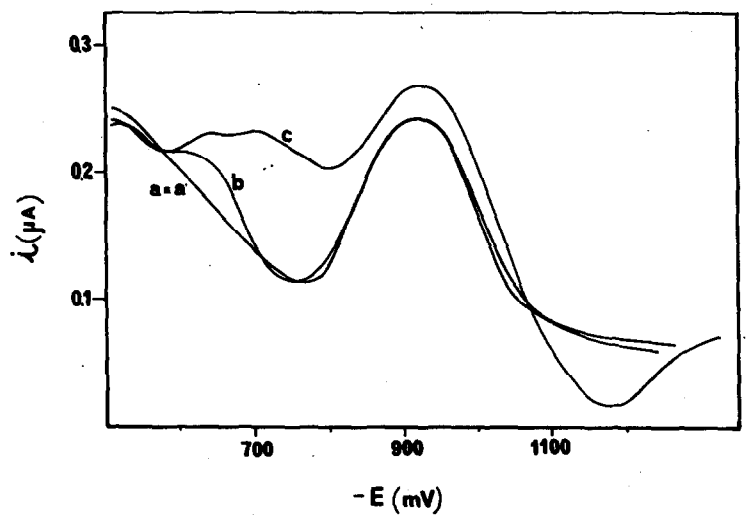

Fig. 4. Voltammogram (dpp) of SO_2 ($3.6 \times 10^{-4}M$) in the presence of various H_2S concentrations: (a') $C_{H_2S} = 0$; (a) $C_{H_2S} = 1.47 \times 10^{-5}M$; (b) $C_{H_2S} = 3.6 \times 10^{-5}M$; (c) $C_{H_2S} = 8.5 \times 10^{-5}M$.

Table 2.

Sampling solvent*	Volume of air, *l.*	Flux, *l./min*	SO_2, *ppm*	NO_2, *ppm*	NO, *ppm*	NO_x, *ppm*
H_2O	28.5	0.95	1.32	—	—	—
H_2O	20.0	0.67	—	—	—	0.30
DMSO	33.0	1.10	1.48	0.20	0.08	0.28
H_2O	31.0	1.03	0.26	—	—	—
H_2O	18.0	0.60	—	—	—	0.12
DMSO	34.5	1.15	0.30	0.08	0.03	0.11
H_2O	29.0	0.97	0.17	—	—	—
H_2O	18.0	0.60	—	—	—	0.18
DMSO	35.0	1.17	0.20	0.18	0.03	0.21

* Water samples analysed by classical methods; DMSO samples by air method.

The air was bubbled at known flow-rate for 30 min through 30 ml of 0.1*M* lithium chloride solution in DMSO, divided between two absorption vessels connected in series; the absorption solutions were combined for analysis by the method described in this paper. Immediately after this sample had been taken, a second sample was collected in the same place, with the aqueous trapping solutions recommended by Saltzman[17] and Scaringelli *et al.*,[2] which were then analysed spectrophotometrically for NO_x,[17] and for SO_2.[2] Results are collected in Table 2 and are practically the same for both methods.

The SO_2 values are systematically about 10% higher for the DMSO solutions than the water solutions. There is probably greater efficiency of uptake by DMSO. Furthermore, our method allows determination of SO_2, NO_2 and NO in a single operation, whereas two separate water samples are needed because of the mutual interference of SO_2 and NO_x.

Nitrogen oxides in DMSO present interesting aspects with respect to the discharge mechanism, that are now undergoing investigation in our laboratory.

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A STUDY OF COATED-WIRE POTASSIUM-VALINOMYCIN AND SODIUM-MONENSIN ION-SENSING SYSTEMS BY USE OF A CONVENTIONAL FIELD-EFFECT TRANSISTOR

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Summary—Polymer films containing a sodium or potassium ion-selective exchanger were coated onto platinum wire and incorporated into a potentiometric arrangement. Comparative results obtained by utilizing different measuring devices, one a conventional pH-meter and the other a field-effect transistor (FET) in series with an electrometer, are discussed. The linear range of either system is comparable with that of other electrochemical techniques. Possible applications of such a device are described.

In a recent report we discussed the potential of electrochemical biosensors in trace organic analysis.[1] A significant advantage of the use of electrogenic processes at lipid membranes is the possibility of application of such "natural" transducers for obtaining physiological data. An important problem in this area is the facile detection *in vivo* of transmembrane electrical properties, for which the FET device appears to be particularly suitable.

The application of the FET to selective ion-sensing was first suggested by Bergveld[2] in relation to neurophysiological measurements. More recent literature pertaining to the field includes a survey of solid-state chemical sensors,[3] a review of ion-sensitive field-effect transistors (ISFET),[4] and reports on the theory of operation of chemically sensitive semiconductor devices (CSSD)[5] and the fabrication and performance of ISFETs for hydrogen, calcium and potassium ions.[6]

The general principle of operation of the ISFET device is that a known voltage is applied between the source and drain leads, causing a current to flow. The potential to be measured is then applied to the gate lead. The potential, which is generated by standard ion-exchange electrode techniques, causes a proportional change in the current flowing between the source and the drain. These devices combine the advantages of conventional ion-selective electrodes with the useful properties of the FET. The majority of ISFETs reported to date have been applied to the acquisition of physiological data and hence great emphasis has been placed on their miniaturization. This partly explains why such a complex procedure was developed for their fabrication. In the present paper, we report some studies (made with a commercially available FET) of the well-characterized potassium–valinomycin system and of the new monensin-based selective sensor for sodium ion.

THEORY OF FET OPERATION

A conventional MOSFET component (Fig. 1) is formed by placing a metal gate over a thin insulating layer which in turn covers the N-channel of the device. The equations governing the operation of an

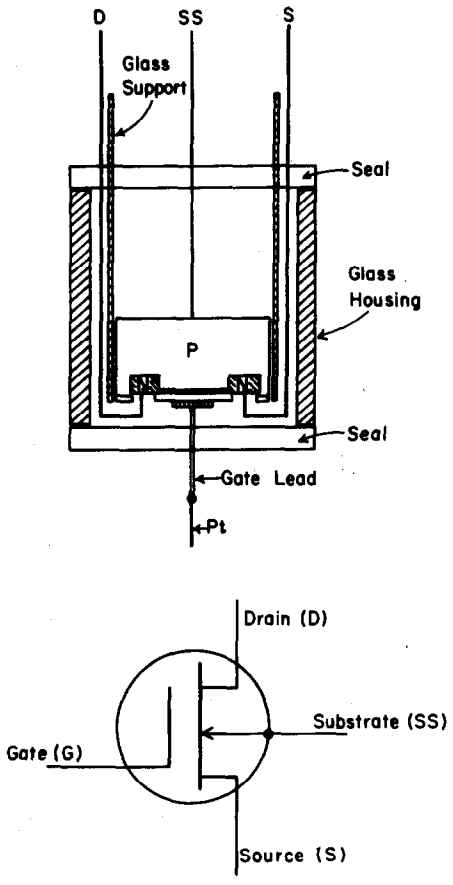


Fig. 1. An N-channel depletion-mode field-effect transistor in a protective casing as used for the experiments described.

FET have been described previously;[7,8] these are applicable to the device described in this work. Additional terms for the ISFET have been derived by Moss *et al.*[6] The drain current (I_D) is given by:

$$I_D \simeq \alpha[(V_G + E - V_T) - \tfrac{1}{2}V_D]$$

where V_G is the potential applied externally to the reference electrode, E is the Nernst potential, V_T is the threshold voltage, V_D is the drain-to-source voltage and α depends on gate capacitance, channel width and length, and on the surface-carrier mobility. It can be shown that the value of V_T applicable in this work is:

$$V_T = E_{ref} + \phi_{C-M} + \Phi_{M-S} - \frac{Q_{ss}}{C_o} + 2\phi_f - \frac{Q_B}{C_o}$$

where E_{ref} is the potential of the reference electrode, Q_{ss} is the fixed surface-state charge density, ϕ_f is the Fermi potential of the substrate and Q_B is the charge per unit area of the surface-depletion region. The additional work terms ϕ_{C-M} and ϕ_{M-S} are the chemical membrane-metal interface work-function difference and metal–semiconductor work-function difference, respectively.

A further important characteristic of the FET device is the leakage current across the gate. This parameter should be as small as possible so that a charge can be efficiently stored across the gate–substrate capacitor. The component chosen for this work has a rated gate leakage of 50×10^{-12} A, which compares favourably with values reported for fabricated devices.[6]

EXPERIMENTAL

Reagents

The electroactive materials used were valinomycin (Sigma, St. Louis, Mo.) and monensin (Eli Lilly, Toronto). Di-n-octyl adipate (DOA) and di-n-octyl phthalate (DOP) plasticizers were of technical grade (Polysciences, Warrington, Pa). All other reagents were of analytical grade and were used without further purification. The polymer support was poly(vinyl chloride) (PVC).

Apparatus

The construction of the FET (RCA 3N-153, N-channel depletion mode, Electrosonics, Toronto) electrode is depicted in Fig. 1. FET drain-current measurements were made with a digital electrometer (Model 616, Keithley, Cleveland, Ohio) incorporated into the circuit shown in Fig. 2. A digital pH-meter (PHM64, Radiometer, Copenhagen) was used for all pH and potential measurements. A single-junction Ag/AgCl reference electrode (Orion, Cambridge, Mass.) was used for all experiments.

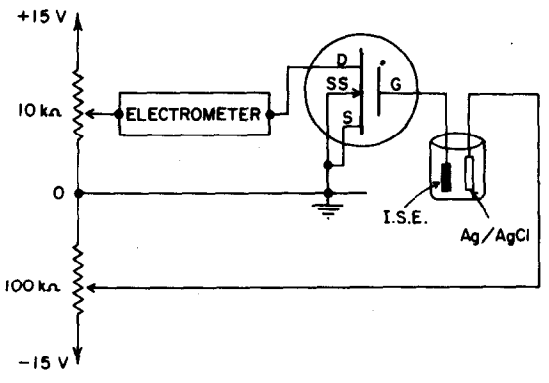
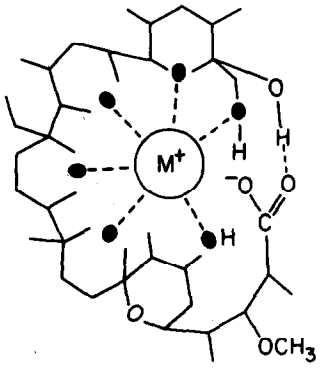


Fig. 2. Electronic circuit incorporating a field-effect transistor.



MONENSIN

Fig. 3. The complex of monensin with a GpIA metal ion.

Procedure

Ion-selective electrodes were prepared by dipping a clean platinum wire into a polymer solution and allowing it to dry in the air. The potassium-selective polymer solution consisted of valinomycin (10.0 mg), PVC (0.33 g) and DOA or DOP (0.89 ml) in tetrahydrofuran (13.0 ml).[9] The dipping was repeated in order to achieve total coverage. Membrane thickness was in the range 100–300 μm, as determined by scanning electron microscopy, and the presence of valinomycin clusters in the smooth polymer surface was visualized by TEM.[10] For the sodium-selective polymer solution, valinomycin was replaced by monensin (25–100 mg), the structure of which is shown in Fig. 3.

The characteristics of the FET were measured in order to determine the optimum operating conditions. The gate lead of the FET was then extended with platinum wire, which was dipped into a potassium-selective polymer solution, as described above. The effect of varying potassium-ion concentration, with and without ionic-strength control, on drain current was then studied. Similar experiments were carried out with the sodium–monensin system.

Parallel experiments were carried out with a standard potentiometric arrangement.

RESULTS AND DISCUSSION

General FET properties

The direct use of the FET for analytical experiments presents the practical problems of susceptibility to damage by an improper lead connection, leading to a short-circuit, and eventual destruction by immersion in aqueous solutions. The design shown in Fig. 1 was employed to overcome these problems and to insulate the FET from air currents and external electrical signals. The FET requires a 10-min warm-up period and has an average working lifetime of one week.

The relationship of drain current to applied gate voltage is shown in Fig. 4. Although the most sensi-

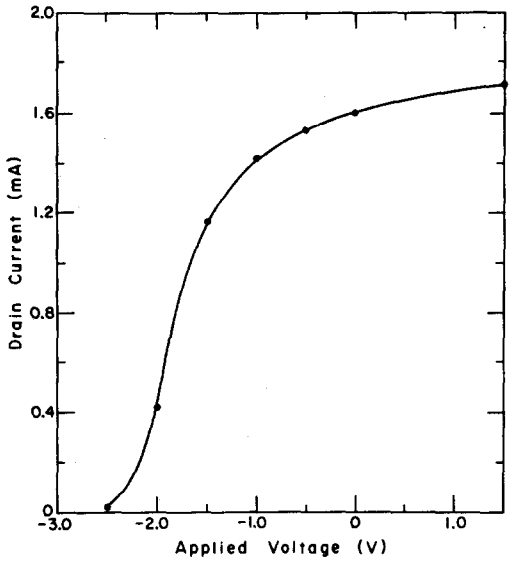


Fig. 4. Drain current *vs.* applied gate voltage for an unmodified field-effect transistor.

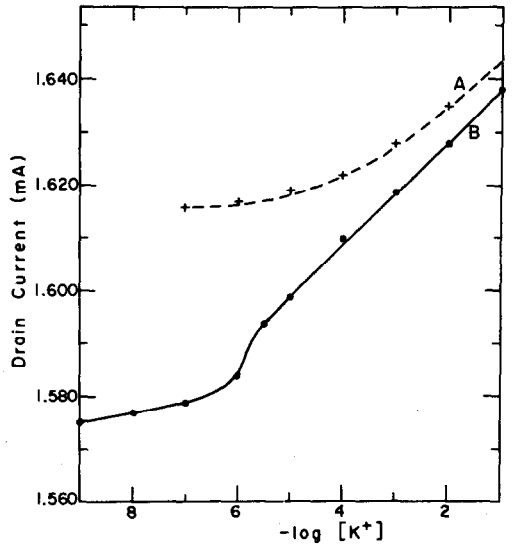


Fig. 6. Drain current *vs.* potassium-ion concentration, A—at constant ionic strength; B—with no background electrolyte.

tive region for drain-current change is between −1.0 and −2.0 V, we operated at zero applied voltage to minimize extraneous electrochemical effects and facilitate correlation with direct potentiometric measurements. The Nernstian response for the FET device in the operating region was 8.2–8.5 μA/pK.

Potassium–valinomycin system

The concentration of the electroactive compound in the polymer as specified above gave an optimum response to potassium ions as indicated by Fiedler and Růžička.[11] An increase in concentration did not significantly increase the potential due to potassium ions.[12]

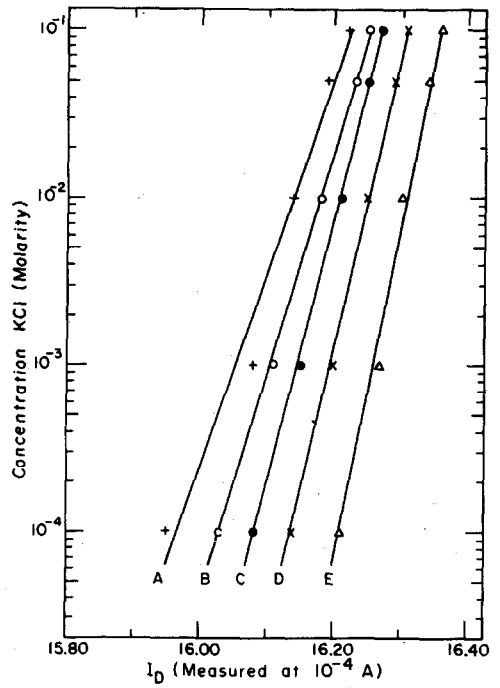


Fig. 5. Drain current *vs.* potassium-ion concentration for a series of polymer coatings. Thickness increases from A to E.

The application of various thicknesses of polymer to the platinum lead significantly affected the potential developed at the gate of the FET. Figure 5 shows the relationship between drain current and potassium-ion concentration for a series of polymer coatings. These results can be explained in terms of two capacitors: the insulator separating the N-channel from the gate metal and the insulator (PVC) separating the platinum base metal from the solution. The two in series will charge to values proportional to their capacitance, thus distributing derived charge and effectively reducing the potential obtained at the gate. As polymer thickness increases, the relative change in drain current with potassium-ion concentration will decrease.

Figure 6 shows the response of the FET device to varying potassium-ion concentrations. Curve A shows the FET response to potassium ions in a medium of constant ionic strength (0.1*M* sodium chloride). In terms of linear range this system compared favourably with the standard selective-ion electrode and the fabricated FET.[9] Curve B shows the FET response in the absence of sodium chloride. The increased sensitivity over the linear range is a product of two effects: the varying ion-exchange potential and a varying surface potential, probably a zeta potential derived from a charged double layer at the electrode surface. This would also explain the results at low pK values.

Sodium–monensin system

The antibiotic monensin has been described as a selective carrier for sodium ions across a hexanol membrane. The carboxylic acid group of the receptor

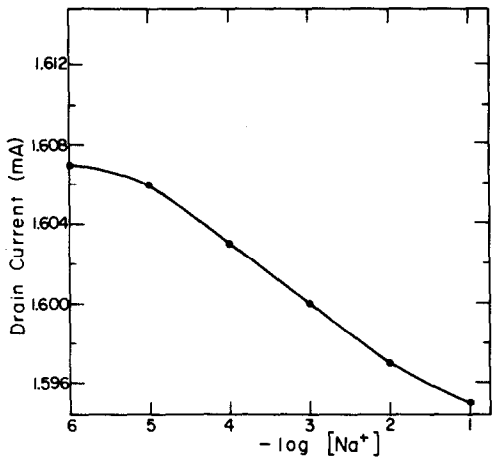


Fig. 7. Drain current *vs.* sodium-ion concentration.

necessitated work with solutions buffered at pH 9.0, and membranes formed from 0.2–0.8% monensin solutions in tetrahydrofuran showed no significant difference in response. After preparation the monensin-containing membranes required initial preconditioning (24 hr) in distilled water to remove membrane-bound sodium ions, and then 5–10 min to equilibrate in the test solution for optimum results.

The response of the monensin-containing polymer to varying sodium-ion concentration in terms of FET drain current and direct potential measurement is shown in Fig. 7 and 8 respectively. The slopes of these curves agree within experimental error, although the slope is less than half that expected for a Nernstian response (*e.g.*, 19.5 ± 0.4 mV/pNa). However the electrode is at least ten times more selective for sodium ions than for potassium ions.

This selectivity is undoubtedly because the sodium complex is more stable than the potassium complex. The potential generated by the sodium–monensin system develops in the opposite direction to that of the potassium–valinomycin system. This can be explained by the fact that when neutral monensin complexes a sodium ion, a hydrogen ion is lost to the solution,

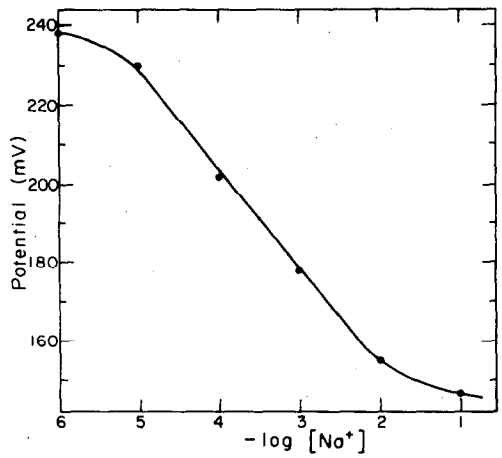


Fig. 8. Potential *vs.* sodium-ion concentration.

and a clathrate-like structure is formed around the sodium ion (see Fig. 3).[13] This shields the positive charge, and a complementary negative charge is distributed between the carboxylic and hydroxyl end-groups of the monensin. As more sodium is complexed, the negative charge perceived is increased, resulting in an increasingly negative electrode potential. Conversely, the potassium–valinomycin system will exhibit a positive increase in potential with increasing potassium-ion concentration owing to the build up of positive (K^+) charge at the membrane surface.

CONCLUSIONS

1. The use of a conventional FET in conjunction with ion-selective exchangers provides a remarkably cheap ($2) and simple method for the selective determination of ions in solution.

2. The polymer-coated wire has a dynamic range comparable with that of the standard ion-selective electrode and the fabricated FET device.[6]

3. In conjunction with the FET, the polymer-coated wire is ideally suited for continual automatic on-site monitoring, and for electronic applications such as control and switching devices, although regeneration of the active species is necessary after a certain time.[6]

4. There is considerable scope for trace organic determinations by using the system described in tandem with selective interactions at artificial membranes.

Acknowledgements—We are very grateful for support for this work from the Natural Sciences and Engineering Research Council of Canada and the Atkinson Foundation of Toronto. Also, we are indebted to Eli Lilly and Co. (Canada) Ltd., Toronto for the provision of a sample of monensin.

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APPLICATION DE L'ANALYSE CALORIMETRIQUE DIFFERENTIELLE A LA DETERMINATION DE LA PURETE DE MEDICAMENTS ORGANIQUES

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Résumé—Les auteurs ont déterminé par analyse calorimétrique différentielle le taux de pureté de quelques médicaments organiques choisis parmi les substances psychothérapeutiques et analgésiques. Après avoir indiqué l'influence de divers paramètres, nature des capsules, vitesse de chauffage, sensibilité, base de temps, ils ont montré la reproductibilité et la fiabilité de cette méthode en effectuant selon un protocole identique cinq déterminations sur chacun des principes actifs.

L'appréciation du taux de pureté des médicaments organiques repose sur deux groupes de méthodes; les unes sont fondées sur l'indentification et le dosage de chacune des impuretés (chromatographie, spectroscopie, polarographie, fluorescence X), les autres telles l'analyse thermométrique en évaluent la quantité totale.

Le principe de l'analyse thermométrique est basé sur la mesure de l'abaissement de la température de fusion provoquée par la présence d'impuretés ou plus récemment par l'étude de la courbe de fusion ou de recristallisation. Cette méthode s'applique à toutes les substances fondant sans décomposition; elle a donné lieu à de nombreux mémoires, en particulier ceux de Cléchet *et al.*[1,2] et de Cisse *et al.*[3] L'analyse calorimétrique différentielle[4,5] occupe une place de choix parmi les méthodes thermométriques; elle offre la possibilité de déterminer la pureté chimique de médicaments à partir de leur courbe de fusion en appliquant l'équation de van't Hoff modifiée. L'application de cette équation est limitée par la concentration en impuretés: selon les auteurs les limites diffèrent 5% pour Davis *et al.*,[6] 2% d'après Joy[7] et 1% selon De Angelis.[8]

Des échantillons d'aminophénazone renfermant de très faibles quantités de phénazone et d'amino-4 phénazone, impuretés rencontrées au cours de l'obtention de ce principe actif, présentent des taux de pureté en accord avec la quantité d'impureté ajoutée pour des teneurs inférieures ou égales à 1%.[9,10] Seules les impuretés formant un eutectique avec le composé principal seraient décelées.

Toutefois selon Marti,[11] dans le cas de formation de solution solide il serait possible d'utiliser cette méthode, le diagramme de phase composé principal–impureté apportant des données relatives aux possibilités et conditions d'application.

Il est possible d'estimer la pureté d'un principe actif par examen visuel de sa courbe de fusion,[9,12] comparativement à celles obtenues dans les mêmes conditions opératoires pour des échantillons de taux de pureté connu compris entre 98,8 et 99,8%, limites admises par les Pharmacopées.

Le présent mémoire rapporte les résultats relatifs à diverses substances psychothérapeutiques et analgésiques dont le comportement thermique a été préalablement étudié.[13,14]

PARTIE EXPERIMENTALE

Appareils

Analyseur thermique différentiel Du Pont de Nemours 990 avec le module pour analyse calorimétrique différentielle dont le principe a été décrit par Baxter.[4]

Appareil Mettler à détermination automatique de la fusion composé du four FP 51, du programmateur FP 52 et de l'enregistreur GA 11.

*Composés étudiés**

Parmi les médicaments psychothérapeutiques, figurent des antipsychotiques, chlorhydrate de chlorpromazine (I), chlorprothixène (II), des anxiolytiques, phenprobamate (III) médazépam (IV), des antidépresseurs, chlorhydrate de clomipramine (V), d'imipramine (VI), d'amitriptyline (VII). La phénazone (VIII) et deux de ses dérivés l'aminophénazone (IX) et l'amino-4 phénazone (X), ont été également étudiés. Toutes les substances médicamenteuses sont conformes aux normes des Pharmacopées Française et Européenne.

Comportement thermique

Le comportement thermique des composés soumis à des cycles chauffage–refroidissement lent et rapide a fait l'objet d'une étude préalable par des méthodes différentes dans leur principe: analyse calorimétrique différentielle, analyse thermique différentielle, thermomicroscopie, mesure de la transparence.

Les résultats en relation avec la détermination de la pureté peuvent être ainsi résumés. Au cours du premier

* Ces produits ont été fournis aimablement par les Laboratoires Ciba–Geigy (V et VI), Roche (II, IV, VII), Paillusseau (III), Specia (I). La phénazone et l'aminophénazone sont des produits commercialisés par la Coopération Pharmaceutique de Melun, l'amino-4 phénazone est un produit Carlo Erba.

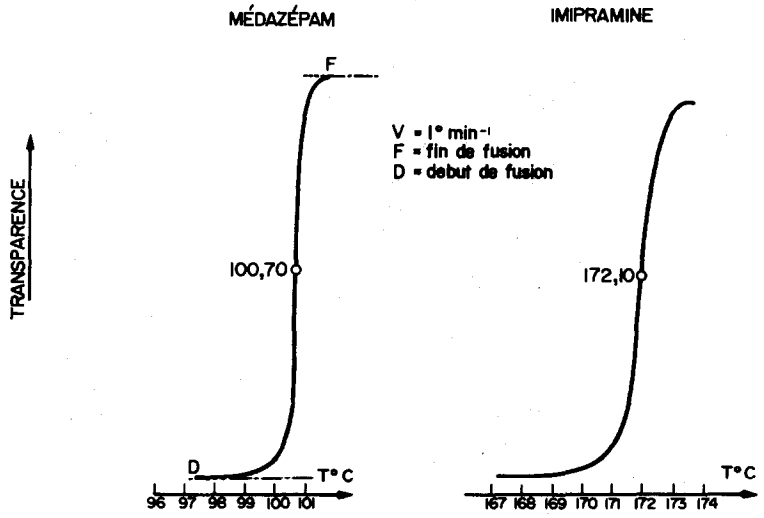

Fig. 1. Courbes de fusion obtenues par enregistrement de la modification de la transparence.

traitement thermique il n'est pas observé de changement de phase solide–solide pour aucune des substances précédemment citées.

La plupart d'entre elles présentent une solidification vitreuse, la recristallisation intervenant par chauffage. Lors de la recristallisation du composé fondu et selon les conditions de refroidissement apparaisent très souvent des formes cristallines différentes.

Tous les médicaments envisagés possédant des formes polymorphes sont commercialisés sous la forme la plus stable à haute température.

La courbe de fusion correspondant au premier traitement thermique des substances commercialisées a été exploitée.

Les courbes de fusion obtenues par enregistrement de la modification de la transparence (Fig. 1), lors de la fusion, permettent d'évaluer avec précision la température et l'intervalle de fusion, différence entre la début et la fin du changement de phase solide liquide.

Les résultats obtenus dans les conditions opératoires suivantes, chauffage à la vitesse de 1°/min, température de début de chauffage T_0 inférieure de 5° à celle de la fusion T_f, sont rapportés dans le tableau 1.

Les courbes de fusion en fonction de la transparence renseignent sur la température et le domaine de fusion dont la connaissance facilite le choix des conditions opératoires pour la détermination de la pureté par analyse calorimétrique différentielle.

Mode opératoire

Les échantillons sont homogénéisés par trituration au mortier d'agate et les substances préalablement conservées 24 h sous anhydride phosphorique. Les prises d'essai sont généralement comprises entre 1,5 et 5 mg selon l'enthalpie de fusion et la sensibilité choisie. Les capsules ordinaires ou hermétiques serties sont choisies selon la stabilité thermique de la substance étudiée après fusion.

La température de départ est inférieure de 3 à 4 degrés à celle de la fusion, la vitesse de chauffage programmée à 1°/min généralement. Toutefois des vitesses de chauffage de 10°/min sont exceptionnellement retenues pour des substances peu stables thermiquement au voisinage de la température de fusion.

La choix de la base de temps est défini par l'étendue du domaine de fusion par suite des conditions imposées par le type d'enregistreur utilisé.

Ainsi dans le cas du médazépam la vitesse de déplacement des plumes de l'enregistreur a été choisie à 0,2 min/pouce compte tenu de la valeur de l'intervalle de fusion inférieure à 2,5; pour les autres substances elle a été réduite à 0,5 min/pouce.

Tableau 1. Températures et intervalles de fusion déterminés à l'aide de l'appareil Mettler

	T_f, °C	Intervalles de fusion, °C
Chlorhydrate de chlorpromazine	195,8 ± 0,1	3,3 ± 0,2
Chlorprothixène	96,9 ± 0,1	2,9 ± 0,4
Phenprobamate	103,3 ± 0,1	3,5 ± 0,2
Médazépam	100,6 ± 0,2	2,2 ± 0,1
Chlorhydrate d'imipramine	172,1 ± 0,2	3,3 ± 0,2
Chlorhydrate de clomipramine	193,5 ± 0,1	3,3 ± 0,3
Chlorhydrate d'amitriptyline	195,3 ± 0,1	3,5 ± 0,3
Phénazone	110,2 ± 0,1	2,2 ± 0,4
Aminophénazone	106,8 ± 0,1	2,6 ± 0,3
Amino-4 phénazone	107,9 ± 0,1	4,6 ± 0,5

La courbe de fusion d'une substance de référence, l'indium, d'enthalpie de fusion connue 6,79 mcal/mg, est réalisée dans les mêmes conditions opératoires. La relation suivante permet d'évaluer l'enthalpie de fusion d'un composé

$$\Delta H_f = \frac{\Delta H_{f(In)} \times \text{Poids}_{(In)}}{\text{Aire courbe fusion}_{(In)}} \times \frac{\text{Aire courbe fusion}_{(X)}}{\text{Poids}_{(X)}} \times PM_X$$

X = substance d'enthalpie de fusion inconnue
PM_x = poids moléculaire de la substance X

Les aires peuvent être mesurées à l'aide d'un planimètre ou par pesée.

RESULTATS

La présence de formes polymorphes après recristallisation du composé préalablement fondu oblige très souvent à utiliser la courbe obtenue lors du premier traitement thermique; une solidification vitreuse nécessiterait de porter le produit fondu à sa température de recristallisation. La fréquence de ces phénomès conduit à prendre en considération la première courbe de fusion du produit commercial.

Influence des conditions opératoires

Le choix des conditions opératoires a pour objectif l'obtention de courbes exploitables quant à leur surface, étalement et ligne de base. Ces différents paramètres sont fonction de la prise d'essai en relation directe avec l'enthalpie de fusion, du choix de la vitesse de déplacement des plumes de l'enregistreur, base de temps, et de celui de la sensibilité en mcal/pouce.

Capsules

L'emploi des capsules hermétiques a été limité aux composés volatils ou à ceux qui, après fusion se décomposent en altérant la tête de mesure. De plus ces capsules présenteraient une résistance thermique plus élevée que les capsules normales. L'emploi des capsules hermétiques a été retenu pour le chlorprothixène; afin d'assurer un meilleur contact thermique la face convexe du couvercle doit être en contact avec l'échantillon. La valeur moyenne du taux de pureté de ce composé a été évaluée à partir de cinq manipulations effectuées sur le même échantillon commercial; l'enthalpie de fusion est déterminée comparativement à celle de l'indium: taux de pureté 99,83 ± 0,03%; enthalpie de fusion 6,83 ± 0,23 kcal/mole.

Les capsules normales permettant par sertissage un excellent contact entre la surface métallique et la substance, ont été utilisées pour tous les autres composés étudiés.

Sensibilité

Le choix de la sensibilité à laquelle il convient d'opérer s'effectue en fonction de l'enthalpie de fusion du produit et du tracé de la courbe de fusion dont la surface doit couvrir une partie importante de la feuille d'enregistrement. Elle peut être réglée de 0,01 à 10 mcal/pouce. La sensibilité de 0,2 mcal/pouce a été principalement retenue.

Base de temps

Les courbes sont enregistrées en prenant pour abscisse le temps exprimé en min/pouce et en ordonnée la quantité de chaleur en mcal/pouce. Les plumes de l'enregistreur sont solidaires d'un bras se déplaçant selon l'axe du temps; leur vitesse de déplacement tient compte dù domaine de fusion à la vitesse de chauffage de 1°/min. Connaissant la vitesse de chauffage et la base de temps, la température de l'échantillon est évaluée sur l'axe des abscisses. Par exemple la base de temps fixée à 0,2 min/pouce représente un déplacement de 5 pouces/min. La vitesse de chauffage étant de 1°/min un degré correspond à 5 pouces; ainsi sont évaluées les températures de fusion des fractions de substances fondues.

La valeur moyenne du taux de pureté du médazépam et l'intervalle de confiance ont été calculés en utilisant les résultats de cinq manipulations effectuées sur des prises d'essai de 3 à 4 mg taux de pureté 99,66 ± 0,14%; enthalpie de fusion 5,14 ± 0,18 kcal/mole.

Vitesse de chauffage

La vitesse de chauffage est choisie la plus faible possible afin d'assurer un excellent équilibre thermique. La vitesse de 1°/min peut être généralement retenue pour les substances stables au voisinage de leur température de fusion. Afin de noter l'influence éventuelle de la vitesse de chauffage cinq manipulations ont été réalisées à 1 et 2 deg/min dans le cas du chlorhydrate d'imipramine dans les conditions retenues: capsules ordinaires, base de temps 0,5 min/pouce, sensibilité 0,2 min/pouce: les valeurs du taux de pureté sont 99,76 ± 0,11 et 99,69 ± 0,28% respectivement pour des vitesses de chauffage de 1 et 2 deg/min.

La comparaison des intervalles de confiance est en faveur du choix d'une vitesse de chauffage de 1 deg/min.

Fiabilité de la méthode

En vue d'apprécier la reproductibilité des résultats nous avons défini les conditions opératoires suivantes: prise d'essai: 2,50 à 5,40 mg; base de temps 0,5 min/pouce; vitesse de chauffage 1 deg/min, appliquées à diverses substances dont le comportement thermique étudié antérieurement laisse apparaître une stabilité au voisinage de la température de fusion.

A titre d'exemple nous indiquons le mode d'évaluation du taux de pureté et de l'enthalpie de fusion du chlorhydrate d'imipramine et du chlorhydrate de chlorpromazine.

Tableau 2. Température de fusion en fonction de $1/F$, inverse de la fraction de substance fondue

$1/F$	Température de fusion après correction, °C
3,45	171,60
3,95	171,55
4,46	171,50
4,88	171,45
5,40	171,40
5,90	171,35
6,35	171,30
6,82	171,25
7,31	171,20

Chlorhydrate d'imipramine

Les courbes de fusion d'un échantillon de ce principe actif et de l'indium de référence, réalisées dans les mêmes conditions expérimentales sont interprétées selon Plato et Glàsgow.[12] La prise d'essai est amenée rapidement à 5° au-dessous de la température de fusion puis, dès stabilisation, chauffée à la vitesse de 1 deg/min.

Les températures sont ensuite corrigées en se référant aux rectifications imposées par l'utilisation des thermocouples (3° au voisinage de 171,7°) et définies par le constructeur.

Les valeurs de $1/F$ et les températures corrigées donnent une ligne droite (tableau 2) de pente égale à 0,105. L'enthalpie de fusion ΔH_f est de 6,87 kcal/mole et la température de fusion corrigée du produit pur est 172°.

En exprimant l'enthalpie de fusion en cal/mole la fraction molaire d'impureté est donnée par l'équation:

$$x_2 = \frac{\Delta H_f}{RT^2}$$

R = constante des gaz parfaits

T = température de fusion du produit pur, en Kelvin.

Dans l'exemple choisi:

$$x_2 = 0{,}105 \times 6870/1{,}98 \times 445^2 = 0{,}0018.$$

Le taux de pureté exprimé en % est 99,82.

Les déterminations effectuées sur cinq prises d'essai d'un même échantillon ont donné les résultats: 99,69; 99,84; 99,75; 99,87; 99,68; écart type 0,11%. Les enthalpies de fusion évaluées sur les mêmes prises d'essai sont: 6,87; 6,78; 6,98; 7,00; 6,90 kcal/mole; écart type 0,09 kcal/mole.

Chlorhydrate de chlorpromazine

Pour la plupart des composés étudiés parmi lesquels le chlorhydrate de chlorpromazine, la représentation graphique de $1/F$, inverse de la fraction fondue, en fonction de la température conduit à une ligne incurvée (Fig. 2). Il est donc nécessaire de linéariser en ajoutant au numérateur et au dénominateur une

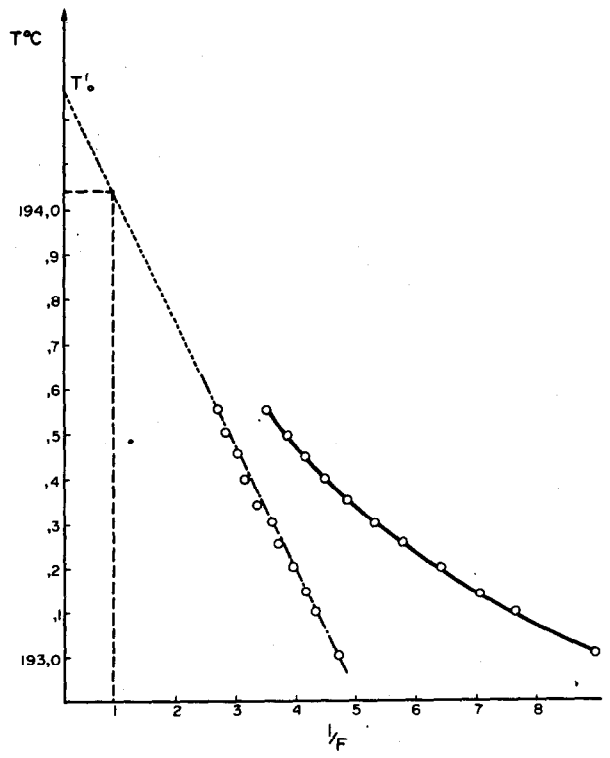

Fig. 2. Courbe de l'inverse de la fraction de substance fondue en fonction de sa température de fusion avant et après linéarisation.

Tableau 3. Taux de pureté, température et enthalpie de fusion des substances étudiées

Substances étudiées	T_f, °C (ACD)	Taux de pureté, % Acidimétrie en milieu non aqueux	Taux de pureté, % ACD	Enthalpie, *kcal/mole*
Chlorhydrate de chlorpromazine	194,3	99,8	99,61 ± 0,19	6,83 ± 0,11
Chlorprothixène	96,8	99,7	99,83 ± 0,03	6,75 ± 0,19
Phenprobamate	103,3	99,7	99,67 ± 0,06	6,63 ± 0,13
Médazépam	100,6	99,8	99,66 ± 0,14	5,14 ± 0,18
Chlorhydrate d'imipramine	172,0	99,5	99,76 ± 0,11	6,90 ± 0,09
Chlorhydrate de clomipramine	193,4	100,3	99,77 ± 0,09	7,50 ± 0,12
Chlorydrate d'amitriptyline	195,2	99,6	99,45 ± 0,20	7,53 ± 0,12
Phénazone	110,0	99,8	99,81 ± 0,09	6,47 ± 0,12
Amino-4 phénazone	107,8	99,7	99,75 ± 0,10	5,95 ± 0,14
Aminophénazone	106,6	99,8	99,77 ± 0,10	6,58 ± 0,15

même quantité ce qui correspond à corriger la ligne de base. La droite coupe l'axe des températures au point de fusion réel du composé pur, la température de fusion de l'échantillon étant donnée par l'intersection avec la parallèle à l'axe des températures pour la valeur $1/F$ égale à 1 (Fig. 2). Les valeurs de l'enthalpie de fusion sont calculées en tenant compte de la linéarisation.

L'analyse calorimétrique différentielle permet d'évaluer le taux de pureté ainsi que l'enthalpie et la température de fusion du produit pur; les résultats relatifs aux différentes substances étudiées sont indiqués dans le tableau 3.

Les valeurs moyennes ont été calculées à partir de cinq déterminations réalisées sur un même échantillon (seuil de probabilité 0,05).

Les températures de fusion déterminées par modification de la transparence sont connues avec une bonne précision; elles diffèrent faiblement de celles obtenues par analyse calorimétrique différentielle. La mesure de la transparence constitue une méthode spécifique d'évaluation de la température de fusion.

L'examen des résultats met en évidence la reproductibilité de la méthode dans les conditions opératoires retenues. Les substances étudiées présentent par analyse calorimétrique différentielle et par acidimétrie en milieu non aqueux, un taux de pureté supérieur à 99%, valeur exigée par les Pharmacopées. L'écart parfois observé dans les résultats donnés par ces méthodes peut s'expliquer par la différence de leur principe.

Par analyse calorimétrique différentielle en effet, seules sont prises en compte les impuretés conduisant à une fusion eutectique avec le principe actif. Ainsi la détermination de la pureté intrinsèque nécessite la connaissance des impuretés principales afin de savoir s'il existe une fusion eutectique ou s'il se forme une solution solide; dans ce dernier cas seul l'établissement du diagramme de phase principe actif–impureté permettrait de préciser les conditions d'application de l'analyse calorimétrique différentielle.

En conclusion la grande sensibilité de la méthode permet de déceler la fusion eutectique. L'intérêt pratique de l'établissement d'abaque, à partir de courbes de fusion obtenues par analyse calorimétrique différentielle a été rappelé; l'examen de la courbe de fusion d'une substance comparativement à l'abaque permet d'estimer rapidement et avec précision des taux de pureté compris entre 99,00 et 99,80%.

La reproductibilité et la fiabilité de l'analyse calorimétrique différentielle viennent s'ajouter, malgré ses limites, aux avantages appréciables de cette méthode: exécution rapide, faible quantité de produit mise en jeu, précision pur les taux de pureté exigés par les Pharmacopées. Elle est de ce fait susceptible de connaître de plus larges applications dans le domaine de l'analyse des substances organiques et plus particulièrement des médicaments.

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Summary—The authors have determined by differential scanning calorimetry the degree of purity of some organic psychotherapeutic and analgesic drugs. The influence of parameters such as type of cup, heating rate, sensitivity, time-base is discussed and the utility and reproducibility illustrated by five determinations, under the same conditions, on each drug.

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SHORT COMMUNICATIONS

DETERMINATION OF *d*-BIOTIN AT THE MICROGRAM LEVEL

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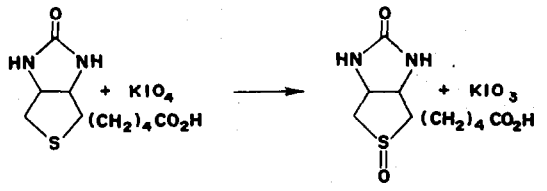
Summary—The iodate formed in the reaction of *d*-biotin with periodate is determined by reacting it with iodide and titrating the iodine with thiosulphate (to determine 90–950 μg of biotin), or the tri-iodide is measured spectrophotometrically to determine 20–80 μg of the test compound. Excess of periodate is masked with molybdate.

Biotin (vitamin H) is necessary for the growth of animals. It has been determined by weighing dried mycelia, and using the weight as a measure of growth, related to the concentration of biotin.[1] Davidek[2] prepared the nitroso derivative with alkali metal nitrite in acid solution and evaluated it polarographically. Avidin yields a new absorption band with certain anionic dyes, but biotin complexes with avidin and reverses this change, which can be followed spectrophotometrically.[3,4] A colorimetric method is based on the condensation of biotin with 4-dimethylaminocinnamaldehyde to yield a coloured product.[5]

Some methods involve reaction of the sulphide group of biotin. Plinton *et al.*[6] determined the substance by oxidation with potassium iodate to a sulphone; after reaction for 30–40 min at 60° the liberated iodine was extracted and measured colorimetrically.

In the present work the reaction of biotin with periodate has been investigated and found to yield a sulphoxide:



The periodate left after reaction with biotin can be determined by reaction with an excess of arsenite, the residual amount of which is titrated with iodine. As only two equivalents of periodate are consumed in the reaction, the resulting difference of two large numbers causes inaccuracy in the determination. It would be more satisfactory and more sensitive to determine the iodate formed (by reaction with iodide and titration with thiosulphate) as each mole of biotin would then give rise to 6 moles of iodine atoms. This can be achieved if the excess of periodate is masked with molybdate at pH 3 to form the heteropoly acid, 6-molybdo-1-periodic acid. Under these conditions only iodate, which does not form a heteropoly acid, reacts with iodide. This observation[7,8] has been applied to the detection and determination of *vic*-diols,[9] iodide[10], α-amino-alcohols[11] and manganese(II).[12]

EXPERIMENTAL

Reagents

*Potassium metaperiodate solutions, 0.1 and 0.01*M. Prepared by dissolving metaperiodate previously recrystallized from water, and stored in a dark-coloured glass bottle.

Ammonium molybdate solutions, 20% and 3%. Prepared by dissolving $(NH_4)_6Mo_7O_{24}.4H_2O$ in water.

*Potassium iodate solution, 1.00 × 10⁻⁴*M.

*Potassium iodide solution, 0.5*M.

Buffer solution. A 0.5*M* sodium chloroacetate solution adjusted to pH 3 with dilute hydrochloric acid.

*Sodium thiosulphate solution, 0.002*M. A 0.01*M* stock solution suitably diluted and solution standardized with potassium iodate solution of equivalent strength.

A chromatographically pure sample of *d*-biotin was used. A standard solution was prepared by dissolving 9 mg of it in 100 ml of water containing about 20 mg of sodium bicarbonate, and diluted as required.

Procedures

Visual titration. The aqueous sample (1–10 ml, containing 90–950 μg of *d*-biotin) is taken in a 150-ml Erlenmeyer flask and diluted to 15 ml. Periodate (5 ml of 0.1*M* solution) is added, the contents are swirled and allowed to stand for 10 min at room temperature. Freshly prepared 20% ammonium molybdate solution (5 ml), 5 ml of buffer solution and about 0.5 g of potassium iodide are added and the flask is again left for about a minute. The liberated iodine is titrated with 0.002*M* thiosulphate, 1–2 ml of 0.5% starch solution being added near the end-point. The whole procedure is applied in a blank determination on distilled water.

Spectrophotometric assay

Preparation of calibration curve. Into 50-ml standard flasks 0.5–5 ml portions of potassium iodate solution are mixed with 2 ml of 10^{-2}*M* periodate, 10 ml of 3% molybdate and 2 ml of buffer solution, and diluted to about 35 ml with water. Iodide solution (10 ml) is added

Table 1. Determination of *d*-biotin by visual titration (1 ml of 0.002*M* thiosulphate ≡ 81.4 μg of biotin)

Biotin taken, μg	No. of detns.	Average recovery, %	Standard deviation, %
93	8	101.9	1.8
188	12	99.9	1.2
280	5	99.7	0.5
371	6	99.9	0.3
476	7	99.6	0.2
554	8	99.8	0.2
652	10	99.7	0.3
758	6	99.7	0.2
846	8	99.6	0.3
930	10	98.5	0.4

Table 2. Spectrophotometric determination of *d*-biotin

Biotin, μg		No. of detns.	Relative std. devn., %
Taken	Found		
21.3	22.4	7	0.6
32.4	31.2	8	0.4
46.3	46.6	6	0.3
52.1	51.9	8	0.2
69.7	69.2	7	0.3
81.6	82.1	7	0.2

and the solution diluted to the mark with water. After 30 min the absorbance of the tri-iodide ion is measured at 350–352 nm in 1-cm cells, against a reagent blank (*i.e.*, without iodate). The absorbance is plotted *vs.* iodate concentration.

Determination of d-*biotin.* An aqueous test sample (0.2–1 ml, pH 6.5–8.0, containing 20–80 μg of *d*-biotin) is mixed with 2 ml of $10^{-2}M$ periodate in a 50-ml graduated flask. The neck of the flask is washed with sufficient water to bring the volume to about 5 ml and the contents are shaken and left for 20 min. Molybdate solution (10 ml, 3%), 5 ml of buffer solution and 10 ml of iodide solution are added and after 30 min the volume is made up to 50 ml and the absorbance is measured in a 1-cm cell *vs.* a reagent blank. The molar concentration of biotin is the same as that of iodate found.

RESULTS

In the earlier methods of determining *d*-biotin, a large excess of periodate is used, which is almost impossible to evaluate by conventional iodometry. The iodate formed by reduction of periodate can be determined after masking the latter with molybdate at pH 3. The method is sensitive, accurate and simple (Tables 1 and 2). Biotin reacts with iodate only in acid medium.

Citric acid, glycine and alanine in up to 10-fold w/w ratio to biotin do not interfere. Glucose, glycerol, methionine, cysteine and thiourea interfere even when present in traces.

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DETERMINATION OF CHLORINE IN SILICATE ROCKS BY ION-EXCHANGE CHROMATOGRAPHY AND DIRECT POTENTIOMETRY WITH AN ION-SELECTIVE ELECTRODE

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Summary—The method has been developed for determination of chlorine in silicate rocks by ion-exchange chromatography and an ion-selective electrode.

An accurate and convenient method for the determination of chlorine in sedimentary rocks was needed for geochemical investigation of sedimentary processes.[1] Among various methods for determination of chlorine in silicate rocks, neutron-activation analysis (NAA), with its high sensitivity and accuracy, has been considered to be the most reliable.[2] However, though the results obtained are reliable, NAA is not suitable for routine analysis of geological samples. Recently, it was reported that the ion-selective electrode is applicable to the determination of chlorine in silicate rocks.[3] It has also been used as a detector in chromatography.[4] In the present work, we show that the two uses can be combined.

EXPERIMENTAL

Redistilled water and guaranteed-reagent grade inorganic chemicals were used throughout. Dowex 1 X-10 (100–200 mesh, Cl^--form) was converted into the NO_3^--form. An Orion Model 94-17 chloride electrode and Model 90-02 double junction reference electrode were used, and an Orion Model 701/digital pH-meter combined with a Hitachi QPD 53 type recorder was also used. The chromatographic column was 7 mm in bore and 8 cm long. The apparatus for ion-exchange chromatography is shown in Figs. 1 and 2.

Procedure

The powdered sample (0.500 g) is fused in a platinum crucible with 4.00 g of sodium carbonate at 980–1000° for 30 min and the fusion cake is dissolved in *ca.* 30 ml of water. The solution is neutralized by adding 5.5 ml of concentrated nitric acid, and digested for 2–3 hr at 60–70°. The solution is filtered through a porosity-4 glass filter, and the volume of filtrate adjusted to 50 ml. A standard solution is prepared in the same way with silica (0.500 g) and a known amount of chloride (added as sodium chloride solution by microsyringe). About 10 ml of the sample solution are transfered onto the column at the injection port by syringe. Chloride is eluted from the column with 0.5*M* sodium nitrate[5] at a flow-rate of 0.85 ml/min (obtained by adjusting the height of the eluent reservoir). Chloride is determined by comparing the peak heights of the chromatograms of the sample and standard.

RESULTS AND DISCUSSION

Although ion-selective electrodes are indeed selective, interfering ions should be removed in trace analysis. In this work, ion-exchange chromatography was used for this purpose, and it was confirmed that there was no response of the electrode to hydroxide ion at pH less than 11.5. Up to 1000 μg each of fluoride, carbonate, phosphate, sulphate, nitrate, perchlorate and acetate will not interfere with the determination. Under the conditions described, chloride, bromide and iodide can be completely separated.

The calibration curve obtained by plotting the peak heights on the chromatogram against the chloride concentrations of the standard solutions was linear

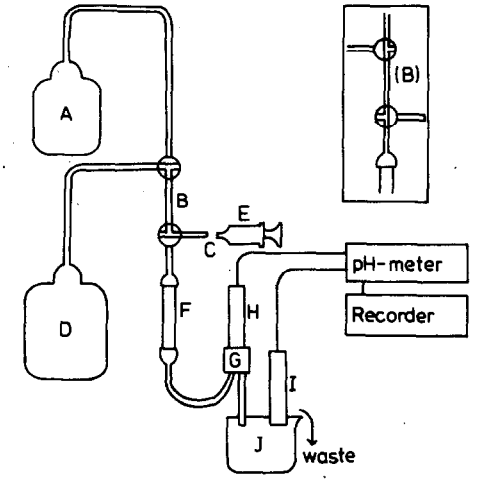

Fig. 1. Schematic diagram of ion-exchange chromatographic system. A, Eluent reservoir; B, sample-charging column (1.0 ml) shown in charging position (flow-through position shown in inset); C, injection port; D, bottle for excess of sample during sample-charging; E, syringe; F, chromatographic column; G, flow-through cap; H, chloride electrode; I, reference electrode; J, beaker (100 ml) bridging the column outlet and the reference electrode.

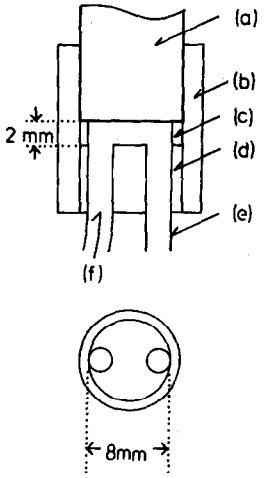

Fig. 2. Flow-through cap details. (a) Chloride electrode; (b) silicone rubber tube; (c) silicone rubber packing; (d) silicone rubber stopper; (e) polyethylene tube; (f) direction of liquid flow.

Table 1. Reproducibility test

Cl found, *ppm*	Mean, *ppm*	Std. devn., *ppm*	Cl found by neutron activation,[7] *ppm*
195, 200 205, 210 220, 225	209	11.6	204

Table 2. Accuracy test

JG-1 (granodiorite), *ppm*	JB-1 (basalt), *ppm*	Analytical method
53	200	This work
54	169	Spectrophotometry[8]*
67	165	Spectrophotometry[9]†
57	190	Neutron activation[1]
60	170	X-ray fluorescence[10]

* Decomposition with condensed phosphoric acid.
† Decomposition by fusion with alkali.

over the range of 0.2–3 ppm; the linearity is in agreement with many other experiments and is also expected theoretically.[6] Reproducibility was tested by using siltstone, and a value of 209 ppm chlorine was obtained as the average of 6 determinations, the coefficient of variation being 5.5% (Table 1). The results agreed well with the value obtained by NAA (204 ppm).[7] An accuracy test based on standard rocks issued by the Geological Survey of Japan is shown in Table 2, in which particularly good agreement of the results obtained by our method with those of NAA can be seen. The results show that the present method is applicable to geochemical studies.

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SIMPLE TITRIMETRIC METHOD FOR THE ANALYTICAL CONTROL OF MACROMOLECULAR POLYPEPTIDES

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(*Received* 15 *February* 1979. *Accepted* 14 *May* 1979)

Summary—A simple potentiometric procedure based on the determination of the primary amino groups in macromolecular polypeptides is presented. The method was found suitable for the detection of decomposition processes involving splitting of the peptide chain (liberation of primary amino groups) and deamination. The method has been applied to analysis of corticotropin fragments ($ACTH_{1-28}$ and $ACTH_{1-32}$), Angiotensin II, and the basic trypsin inhibitor Kunitz base (Trasylol).

Macromolecular polypeptides may split into smaller peptides, and some of their functional groups are also sensitive to oxidation. These changes may decrease the biological activity of the macromolecule. Most of the spectrophotometric[1-3] and chemical[4,5] procedures applied for the analytical control of such products measure the decomposition products together with the undecomposed molecule. The methods based on the determination of the biological activity[10-12] may measure the biologically active decomposition product together with the parent peptide. The course of decomposition can be monitored only by chromatographic and electrophoretic separation processes.[6-9]

However, a simple analytical procedure equally suitable for control analysis of macromolecular peptides and monitoring their decomposition has been developed and is presented here.

The Schiff-base formation reaction applied earlier for the measurement of amino-acids and smaller peptides by Sörensen[13-15] serves as the basis for the new method. The primary amino-groups of polypeptides, present quantitatively in protonated form in a neutral solution, react with formaldehyde to produce Schiff-bases, accompanied by liberation of the protons originally co-ordinated to the nitrogen atoms. The acid liberated in this way is equivalent to the primary amino groups in the sample, and can be titrated.

The original macro method of Sörensen, which used visual end-point detection, has been converted into a semimicro potentiometric procedure suitable for the analysis of pharmaceutical products of low peptide content.

EXPERIMENTAL

The reaction conditions necessary for quantitative Schiff-base formation and deprotonation on the semimicro scale were studied with amino-acids as model systems.

It was shown, that in solutions containing 18% v/v formaldehyde, potentiometric titration with 0.01*M* alkali of the acid liberated in the course of the Schiff-base formation has a reproducibility of ±0.5%. The same was found for macromolecular polypeptides.

Procedure

A quantity of polypeptide or its salt equivalent to 2–3 ml of 0.01*M* sodium hydroxide is dissolved in about 5 ml of distilled water and adjusted accurately to pH 7 with 0.01*M* sodium hydroxide. Then about 5 ml of 35–38% aqueous formaldehyde solution, similarly neutralized, are added. After 30 min, the acid liberated is *slowly* titrated with 0.01*M* carbonate-free sodium hydroxide.

A precision pH-meter (*e.g.*, Radiometer pH M64 Research, reading to 0.1 mV) and an automatic burette (e.g. ABU-12, precision ±0.001 ml) are recommended.

RESULTS AND DISCUSSION

The practical applicability of the method was tested by the analysis of the following macromolecular polypeptides:

(1) the *N*-terminal fragment of synthetic human α_H-corticotropin containing 32 amino-acids ($ACTH_{1-32}$);

(2) the analogous fragment containing 28 amino-acids ($ACTH_{1-28}$);

(3) the basic pancreatic trypsin inhibitor Kunitz base polypeptide (BPTI), containing 58 amino-acids;

(4) Angiotensin II (a polypeptide) containing 8 amino-acids.

From the amino-acid sequences of the corresponding peptides the numbers of free primary amino groups of the undecomposed polypeptides are known. From these numbers, the equivalent weights of the compounds can be deduced. The results of the analyses are summarized in Table 1. The products examined contained as impurity only a small amount of water. This was determined by the Karl Fischer method. The weights in the third column of the table

Table 1. Results of the analysis of polypeptides

Peptide	Equivalent weight	Peptide taken, *mg*	Consumption of 0.01*M* NaOH, *ml*	Peptide found, *mg*	Error, %
$ACTH_{1-32}$ (Corticotropin acetate)	812.8	17.32	2.18	17.68	+2.1
		17.32	2.10	17.07	−1.5
$ACTH_{1-32}$ (Corticotropin hydrochloride)	841.4	18.06	2.05	17.49	−3.1
		17.88	2.20	18.51	+3.5
$ACTH_{1-28}$	697	10.79	1.55	10.80	+0.2
		3.49	0.50	3.49	−0.1
BPTI perchlorate	1523	13.79	0.86	13.10	−2.0
		27.58	1.80	27.41	−0.6
		39.03	2.62	39.90	+2.2
BPTI (Trasylol)	1381.4	22.52	1.65	22.79	+1.2
		22.52	1.63	22.52	0.0
Angiotensin II	1081.5	9.19	0.78	8.96	+2.5
		9.34	0.82	9.42	−0.9

refer to water-free peptide salts. The data exhibit the good reproducibility of the measurements.

The method was also applied successfully in the course of our studies of the co-ordination chemistry of polypeptides,[16,17] to determine the total peptide concentration of the starting solutions.

A characteristic decomposition reaction of polypeptide molecules is hydrolytic chain breaking accompanied by production of new terminal amino and carboxyl groups. There is thus an increase in the number of primary amino groups per mole of peptide.

Hence it was expected that our method could be used to follow the decomposition of polypeptides by hydrolytic chain splitting. For verification, an $ACTH_{1-32}$ sample was partially decomposed with trypsin and the product analysed by the new method and by paper electrophoresis in solutions of pH 2 (acetic acid–formic acid–water mixture) and pH 5.7 (pyridine–acetic acid–water mixture). The electrophoresis results indicated the presence of four decomposition products beside the undecomposed $ACTH_{1-32}$.

When the electrophoresis was repeated with samples taken from different places in the same ACTH product, the intensity ratios of the spots characterizing the decomposition products were found to be different.

The potentiometric analysis of 3 samples also taken from different parts of the product examined, showed the presence of 8.01, 6.46 and 5.71 primary amino groups per ACTH chain. Since the undecomposed $ACTH_{1-32}$ molecule contains 5 primary amino groups and each splitting of the peptide chain results in the formation of one additional terminal amino group, these results also reflected the decomposition of the peptide.

The quantitative splitting of $ACTH_{1-32}$ into four smaller peptides would result in the occurrence of at most 8 primary amino groups per molecule of $ACTH_{1-32}$. The results 8.01, 6.46 and 5.71 amino groups led us to the conclusion that the material decomposed only partially and that the degree of decomposition was different in the various parts of the sample. This explanation is supported by the electrophoresis results. With homogenized samples, the reproducibility of our method was found to be $\pm 1\%$ even for decomposed products.

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DETERMINATION OF FeS_2 IN VENEZUELAN LATERITES AFTER A SULPHURIZATION PROCESS

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Summary—A technique is presented for determination of FeS_2 in Venezuelan laterites after a sulphurization process. The determination is based on a reaction with water followed by a turbidimetric determination of sulphate ions in solution. The effect of the reaction time and of the particle size is investigated. Data are given showing the precision to be better than 3%, and the accuracy was studied by preparation of a series of synthetic samples of FeS_2, FeS and Venezuelan laterite.

The objective of this project was to determine the amounts of FeS_2 and FeS in Venezuelan laterites after a carbon–sulphurization (treatment with a CO_2 and SO_2 gas mixture) reaction. The idea behind the carbon–sulphurization reaction is the separation of iron from laterite, leaving a mixture of principally Al_2O_3, SiO_2 and TiO_2,[1] which can be used instead of bauxite as the raw material for production of aluminium.

In Venezuela, bauxite is relatively scarce compared to laterite, but the laterite contains up to 30% of total iron (as Fe_2O_3).[2] Figure 1 shows the theoretical reaction products from the carbon–sulphurization reaction under different experimental conditions.[1] It can be seen that FeS_2 and/or FeS can be formed. Thus a technique to determine FeS_2 in the presence of FeS was explored and is reported here.

The following reactions[3] were studied as a means of determining FeS_2 indirectly in the presence of FeS:

$$4FeS + 3O_2 + 6H_2O \rightarrow 4\,Fe(OH)_3 + 4S \quad (1)$$
$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2\,FeSO_4 + 2H_2SO_4 \quad (2)$$

Other reactions with dilute and concentrated acids were studied, but without useful results. Also reactions with water and acids were investigated by determination of the iron in solution, but again without success.

EXPERIMENTAL

The reaction with water

Weigh 500 mg of 100–250 mesh sample into a 30-ml plastic beaker and add 10 ml of distilled water. After 30 min reaction time (with occasional stirring) filter with a sintered-glass crucible of fine pore-size (porosity 4). Wash the beaker and precipitate with about 10 ml of distilled

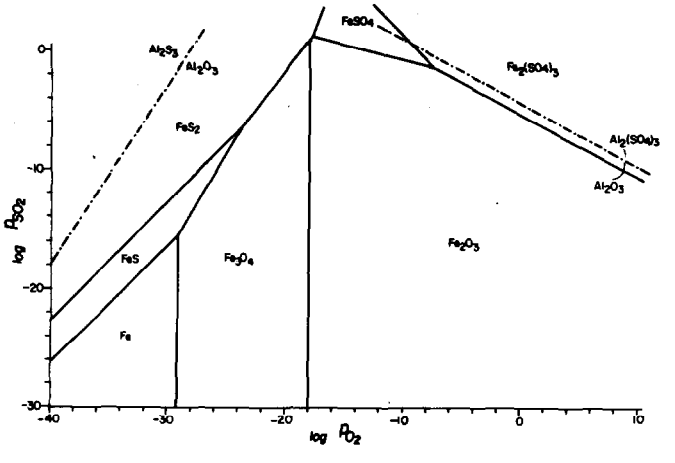

Fig. 1. Phase diagram for Fe–S–O and Al–S–O at 500°C.

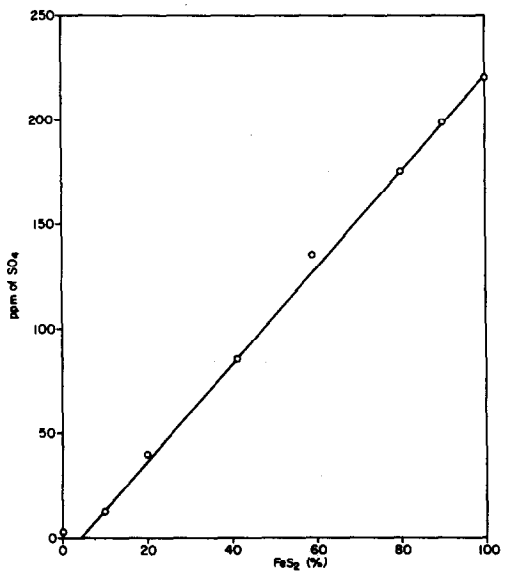

Fig. 2. Calibration curve, plotting ppm of sulphate in the final 25 ml of diluted solution measured, *vs.* per cent FeS_2 in the 500-mg standard samples.

water. Transfer the filtrate to a 25-ml standard flask and dilute to the mark.

Turbidimetric measurement of sulphate

Dilute the sample by a factor of 25 with distilled water to ensure the concentration of sulphate is in the linear range of the calibration curve. Apply any convenient turbidimetric method for sulphate in water, covering the range up to 250 ppm. (We used a Hach Kit portable colorimeter and the "SulfaVer IV" procedure,* in which the requisite dose of the commercial reagent mixture was added to 25 ml of the diluted sample and another 25-ml portion was used as a blank, and 10 min later the absorbance at 450 nm was measured.)

Prepare a calibration curve by use of synthetic samples prepared by mixing known amounts of FeS_2 and FeS. The graph is linear but gives an intercept on the FeS_2 axis (Fig. 2).

RESULTS AND DISCUSSION

Examination of Fig. 2 shows that a 500-mg sample of FeS_2 will produce an apparent sulphate concentration of 220 ppm in the solution measured. As 220 ppm of SO_4^{2-} in 25 ml corresponds to 1.83 mg of sulphur, which is derived from 1/25 of the original solution, and the 500 mg of FeS_2 contains 267 mg of sulphur, the extent to which reaction (2) proceeds is about 17%.

The accuracy of the proposed method was studied by preparing synthetic samples of known amounts of FeS_2, FeS and Venezuelan laterite. The results for the synthetic samples were in excellent agreement with the amounts of FeS_2 taken. The precision was investigated by determination of FeS_2 in 10 separate samples and found to be about $\pm 2\%$ for FeS_2 in the range 10–50%.

Since the reaction rate should be dependent upon the surface area, the effect of different particle sizes was studied. It was found that there is little or no effect in the range 63–250 mesh-size but a particle size finer than 250-mesh would give erroneously high results unless corrected for.

In an experiment to optimize the reaction time it was found that the concentration of sulphate released increases with time up to about 20 min, and then becomes relatively constant. Thus 30 min was decided to be optimum for the reaction time.

Since the Hach Kit procedure suggested that the sulphate should be measured 10–15 min after addition of the reagent, this was checked. The results showed that the reading was constant from 10 min to more than 30 min after introduction of the reagent.

CONCLUSIONS

It has been shown that the proposed method for determining FeS_2 indirectly by the concentration of sulphate after a chemical-phase reaction with water is reproducible to about 2%. This is adequate for chemical-phase analysis but could probably be improved by measuring the sulphate concentration with a laboratory spectrophotometer rather than the portable Hach Kit instrument.

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TITRATION OF PHYTIC ACID

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Summary—Titrimetric assays for phytic acid by titration with iron(III) or thorium are described. Stannous chloride interferes in both systems, causing negative errors directly proportional to the amount of stannous chloride. The thorium:phytate ratio in the complex formed is 2:1, which is interpreted as resulting from the possession of two chelating centres by phytic acid.

Phytic acid and its sodium salt are widely used in diagnostic nuclear medicine as chelating agents for technetium. The acid is obtained in a reasonably pure state from corn steep-liquor and, despite some past uncertainty about its structure, is now assumed to exist predominantly as the geometric isomer *myo*-phytic acid (*cis*-1,2,3,5-*trans*-4,6-inositol hexaphosphoric acid).[1] Examination of a molecular model shows that five of the six orthophosphate groups occupy equatorial positions in the preferred chair conformation. The formula of the sodium salt (dried at 110°) has been established[2] as $Na_{12}C_6H_6P_6O_{24}.3H_2O$ and it is this material which is the agent of choice for commercial preparations.

Conventional methods of analysis for phytic acid have been reviewed;[3] the most widely used procedure remains some modification or other of the titration with iron(III), developed by Heubner and Stadler.[4] That procedure is reported to be reproducible, though based on a non-stoichiometric relationship of 2.8 moles of iron for each mole of phytic acid. Other workers report different relationships.[3]

We have evaluated this technique and have attempted to develop an alternative based on an integral stoichiometric ratio. Since titrations with thorium have proved useful for determination of analagous phosphonate compounds,[5] this approach was pursued. Our major purpose was to produce a procedure for the assay of commercial sodium phytate in radiopharmaceutical preparations which contain stannous chloride as reducing agent.

EXPERIMENTAL

Reagents

Thorium nitrate solution, 0.01 or 0.001*M*, standardized against EDTA.[6]

Xylenol Orange solution, 0.1%.

Ferric chloride solution, Fe(III) 1 mg/ml in 0.05*M* hydrochloric acid (*e.g.*, J. T. Baker "Dilut-It" standard).

5-Sulphosalicylic acid.

Phytic acid, sodium salt (Sigma Chemical). Found: Na, 27.15%; P, 18.81%; theory: Na, 28.21%; P, 19.00%.

Procedure for titration with iron (III)

The sample (dried at 110° overnight) is dissolved in 50 ml of water. Approximately 10 mg of 5-sulphosalicylic acid are added and the solution is titrated with standard ferric chloride solution to the appearance of the first permanent pink colour. The factor used in the calculation is that recommended by Heubner and Stadler.[4]

Sodium phytate (mg) = 6.26 × volume of titrant (ml) × concentration of titrant (Fe, mg/ml).

Procedure for titration with thorium

The sample (dried as above) is dissolved in 50 ml of water, the pH adjusted to 1.9–2.2 with 0.02*N* hydrochloric acid and the mixture heated to 60°. After addition of 1 ml of Xylenol Orange solution, the sample is quickly titrated from yellow-orange to pink.

Sodium phytate (mg) = 489 × volume of titrant (ml) × molarity of titrant.

RESULTS AND DISCUSSION

Our preliminary observations on the thorium titration showed that the metal:phytate ratio in the complex formed was 2:1, so the calculations are based on that ratio. For the titrations with iron(III) our observations confirmed that the factor proposed by Heubner and Stadler was the most valid of those suggested. 5-Sulphosalicylic acid was chosen as an indicator superior to the ammonium thiocyanate originally recommended.[4]

A series of ten determinations of 40.87-mg portions of sodium phytate trihydrate gave 40.6 ± 0.4 mg by thorium assay, and 41.0 ± 1.1 mg by iron(III) assay. The end-point given by Xylenol Orange was judged easier to see than that with 5-sulphosalicylic acid and this is reflected by the better relative standard deviation (1.0% *vs.* 2.6%).

When stannous chloride was added to sodium phytate samples of approximately 10 mg, the nominal amount in commercially available vials of the reagent, interference with both methods was observed (Fig. 1). the results being low by 0.9 mg of sodium phytate trihydrate per mg of stannous chloride present (or 0.176 mole of phytate per mole of stannous chloride). This error was the same for both techniques, suggesting a common mechanism for interference, presumably complexation with phytate. Nonetheless, either technique may be used for routine analysis of commercial preparations, since the error is reproducible and a correction can be applied.

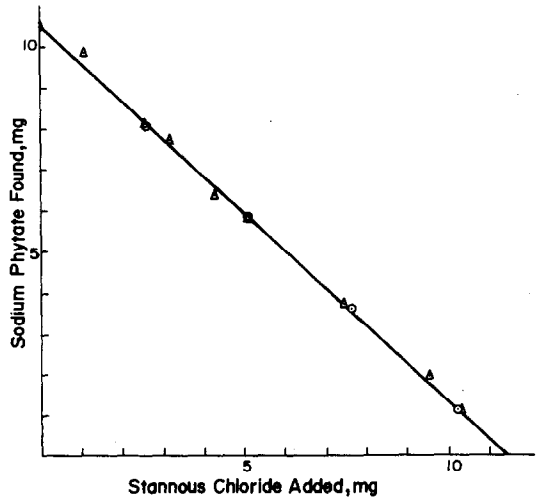

Fig. 1. Effect of stannous chloride on assays of 10.3-mg portions of sodium phytate. Thorium assay (⊙); ferric ion assay (△).

The 2:1 combining ratio of thorium and phytate may be explained by (*a*) the presence of 12 anionic oxygen atoms on each phytate ion and (*b*) the unique geometry of the predominant isomer, and strongly suggests that after chelation of the first thorium ion, phosphate oxygen atoms on the other side of the ring remain available to chelate a second thorium ion. Thus, the fixed geometry of the inositol ring provides a singular example of a chelating agent with two separate complexing centres.

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ORGANIC ANALYSIS WITH A NEW Ag^+-SELECTIVE MEMBRANE ELECTRODE

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Summary—A new Ag^+-selective membrane electrode obtained by impregnating a graphite rod (attached to the end of a Teflon tube) with the silver(I) chelate of 1-(2',3',5'-tri-*O*-benzoyl-β-D-ribofuranosyl)-4-thioxo-5-methylthio-6-azauracil dissolved in chloroform gives a stable and reproducible response to silver in the 10^{-1}–$10^{-5}M$ range with a slope of 60 mV/decade. A new method for determination of some β-chlorovinyl ketones is based on use of the electrode in potentiometric titration of the chloride displaced by tertiary amines from β-chlorovinyl ketones in forming the corresponding quaternary ammonium salts.

Several Ag^+-selective electrodes with liquid membranes have been developed and characterized.[1–5] We now add a new one.

EXPERIMENTAL

Apparatus and reagents

The emf values were measured at room temperature in mechanically stirred solutions, with a digital pH/mV-meter (Prăcitronic, East Germany). The potentiometric titration curves were recorded with an automated outfit composed of a TTT2 Titrator, ABU12 Autoburette and SBR2C Titrigraph recorder (Radiometer). The indicator electrodes used were the Ag^+-selective membrane electrode of our own construction, and Cl^- and Br^- selective electrodes

$$\text{Ag}^+\text{-selective membrane electrode} \left| \begin{array}{l} \text{Ag}^+(C_{\text{Ag}^+}); \\ \mu = 0.5M\ (\text{KNO}_3) \end{array} \right| \begin{array}{l} \text{KNO}_3 \\ \text{satd.} \end{array} \Bigg| \text{SCE}$$

(Radelkis OP-Cl-7112D and OP-Br-7111D). A saturated calomel electrode (type K401, Radiometer) was used as reference electrode, connected to the sample solution through a saturated potassium nitrate bridge.

β-Chlorovinyl ketones were prepared according to Wakayama *et al.*[6] The drugs analysed were of pharmaceutical grade.

RESULTS AND DISCUSSION

The new Ag^+-selective membrane electrode has as liquid membrane the Ag(I) chelate of 1-(2',3',5'-tri-*O*-benzoyl-β-D-ribofuranosyl)-4-thioxo-5-methylthio-6-azauracil, dissolved in chloroform.[7] The reagent, denoted by HR (a weak organic acid), was recently obtained and characterized by Cristescu.[8]

The Ag^+ ions from the aqueous phase and HR from the organic phase are in equilibrium:

$$Ag^+_{aq} + (HR)_0 \rightarrow (AgR)_0 + H^+_{aq} \qquad (1)$$

Following the treatment used previously,[3,4] equation (2) is obtained for the electrode:

$$E = E'_0 + (RT/F) \ln [Ag^+]_{aq} \qquad (2)$$

E'_0 is the conditional standard potential of the electrode *vs.* SCE, obtained by extrapolating the electrode function (Fig. 1) to $pAg^+ = 0$. Its value depends on the concentration of silver in the liquid membrane in the electrochemical cell

where C_{Ag} is the silver concentration in the test solution. The value of E'_0 is related to the concentration of silver in the membrane by $E'_0 \sim (RT/F) \ln (AgR)_0$ and thus also depends on the extraction constant. It is +530 mV when the concentration of silver in the membrane is $5 \times 10^{-4}M$. The basic characteristics of the electrode are given in Table 1.

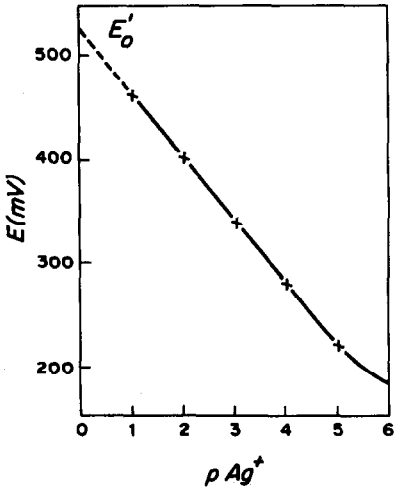

Fig. 1. The electrode function.

* National Institute of Chemistry, Department of Analytical Chemistry, 77208 Spl. Independenţei 202, Bucharest, Romania.

Table 1. The basic characteristics of the Ag^+-selective membrane electrode

Membrane	1-(2′,3′,5′-tri-*O*-benzoyl-β-D-ribofuranosyl)-4-thioxo-5-methylthio-6-azauracil in $CHCl_3$
Concentration of silver complex in the membrane	$5 \times 10^{-4} M$
Slope of the electrode function	60 mV/decade of concentration
Influence of pH	Depends on the Ag^+ concentration
Response time	A few sec in concentrated solutions and approx. 2–3 min in 10^{-4}–$10^{-6} M$ range
Selectivity	The selectivity coefficients calculated by the separate solution method[9] have shown that only Hg^{2+} interferes
Reproducibility of the potential measurements	±4 mV in a 5-week period

ANALYTICAL APPLICATIONS

Determination of β-chlorovinyl ketones

β-Chlorovinyl ketones are a group of organic compounds used as intermediates in the synthesis of a wide range of compounds; they have the general formula R–CO–CH=CHCl (R = alkyl). They can be determined by measuring the halide produced by treatment with alkali. Because the chlorine atom is strongly activated by the carbonyl group in the β-position, the β-chlorovinyl ketones can be decomposed under even milder conditions, for example they react easily with tertiary amines (*e.g.*, Et_3N), forming the quaternary ammonium salts,[10] and these may be directly determined with an Ag^+- or Cl^--selective membrane electrode.

By means of this last property, we have succeeded in monitoring the reduction reaction of β-chlorovinyl ketones (with $NaBH_4$):

$$\underset{\text{(I)}}{R{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH{-}Cl} \xrightarrow[\text{solvent}]{NaBH_4} \underset{\text{(II)}}{R{-}\overset{\overset{OH}{|}}{CH}{-}CH{=}CH{-}Cl} \qquad (3)$$

To determine the β-chlorovinyl ketone (I) in the presence of the reduced compound (II), the reaction

$$\underset{\text{(I)}}{R{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH{-}Cl} + (C_2H_5)_3N \longrightarrow \underset{\text{(III)}}{[R{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH{-}N^+(C_2H_5)_3]Cl^-} \qquad (4)$$

was used to produce the quaternary ammonium salt (III) which may be potentiometrically titrated, in the presence of an Ag^+-selective membrane electrode, after acidification.

The following aspects were considered: (*a*) detection of trace chloride in β-chlorovinyl ketones; (*b*) kinetics of conversion of β-chlorovinyl ketone into the corresponding quaternary ammonium salt with Et_3N as quaternization agent; (*c*) influence (on β-chlorovinyl ketone degradation) of the nature of the acid used for neutralization of the excess of Et_3N (in monitoring the reduction reaction).

The β-chlorovinyl ketones analysed by the method are shown in Table 2. No traces of chloride were found in any of the compounds mentioned in Table 2. It was found that acidification of the sample with $1 M$ nitric acid resulted in degradation by up to 20% within 30 min (see Table 3), so this acid cannot be used for the acidification step in the procedure used for monitoring the quaternization reaction, though it is suitable for determination of total β-chlorovinyl ketone. A 5% acetic acid solution was found the most suitable for the acidification in the monitoring experiment.

To study the kinetics of quaternization we pro-

Table 2. β-Chlorovinyl ketones analysed potentiometrically with ion-selective membrane electrodes

Name	R	Molecular weight	Cl (%)
1-Chloro-1-buten-3-one	CH_3	104.53	33.91
1-Chloro-1-heptan-3-one	C_4H_9	146.62	24.18
1-Chloro-1-octen-3-one	C_5H_{11}	160.64	22.07
1-Chloro-1-decen-3-one	C_7H_{15}	180.70	18.78
1-Chloro-1-tetradecen-3-one	$C_{11}H_{23}$	244.81	14.48

Table 3. Degradation of 1-chloro-1-decen-3-one in HNO_3 medium (taken: 21.65 mg)

Time *min*	Found *mg*	Degradation (%)
5	1.53	7.07
10	2.55	11.78
20	4.08	18.85
30	4.42	20.42
40	4.42	20.42

* The Ag^+-selective membrane electrode was used.

Table 4. Kinetics of conversion of 1-chloro-1-decen-3-one into the corresponding quaternary ammonium salt (taken: 9.62 mg)*

Time *min*	1-Chloro-1-decen-3-one found, *mg*	Conversion (%)
3	8.76	91.0
5	9.41	97.8
10	9.62	100.0
20	9.62	100.0
30	9.64	100.2

* The Ag^+-selective membrane electrode was used.

ceeded as follows: 1 ml of Et_3N was added with stirring to about 10 mg of β-chlorovinyl ketone dissolved in methanol. After a time *t*, the sample was neutralized and then acidified with 5% acetic acid solution and potentiometrically titrated with 0.01*M* silver nitrate.

From Table 4 it is seen that 1-chloro-1-decen-3-one is quantitatively converted into the quaternary ammonium salt in 10 min (similar conversion times were found for the other β-chlorovinyl ketones).

Some results of 1-chloro-1-buten-3-one determinations are shown comparatively in Table 5, and show

Table 5. Potentiometric determination of 1-chloro-1-buten-3-one with ion-selective membrane electrodes

Time (*mg*)	Found, *mg*		Error, %	
	Ag^+-selective electrode	Cl^--selective electrode	Ag^+-selective electrode	Cl^--selective electrode
1.47	1.46	1.46	0.7	0.7
2.94	2.96	2.93	0.7	0.3
4.41	4.43	4.42	0.5	0.2
5.88	5.85	5.91	0.5	0.5
7.35	7.34	7.31	0.1	0.6
8.82	8.85	8.86	0.3	0.5
10.29	10.24	10.26	0.5	0.3

Table 6. Potentiometric analysis of drugs

Pharmaceutical product	Therapeutic form	Composition	Found	
			Ag^+-selective electrode	Br^--selective electrode
Lauronil (Scoponal)	Tablets	1 tablet contains: Scopolaminium hydrobromicum 0.6 mg Acidum phenylaethylbarbituricum 100 mg Excipiens q.s. for one tablet	0.67 mg (average of 2 determinations)	0.67 mg
Scobutil (Buscopan)	Tablets	1 tablet contains: *N*-Butylscopolammonium hydrobromicum 10 mg Excipiens q.s. for one tablet	9.72 mg (average of 7 determinations)	9.75 mg
	Injectable aqueous solution 1-ml ampoule	1 ampoule contains: *N*-Butylscopolammonium hydrobromicum 10 mg Glucosum 50 mg Aqua distillata ad 1 ml	10.85 mg (average of 4 determinations)	10.72 mg
Algo-buscopan	Injectable aqueous solution 5-ml ampoule	1 ampoule contains: *N*-Butylscopolammonium hydrobromicum 0.02 g Noraminophenazonium 2.50 g	0.020 g (average of 7 determinations)	0.021 g

that both ion-selective membrane electrodes give good results for 2–10 mg of the compound.

Determination of scopolamine hydrobromide and N-*butylscopolammonium bromide*

Scopolamine hydrobromide is mainly used for its sedative action in psychiatry and surgery (combined with morphine and barbiturates). The compound *N*-butylscopolammonium bromide obtained from scopolamine by quaternization with C_4H_9Br is recommended as an antispastic drug which causes less side-effects than atropine.

To determine scopolamine hydrobromide in the pharmaceutical product known under the trade names Scoponal and Lauronil and the *N*-butylscopolammonium bromide in the pharmaceutical products Scobutil and Algo-buscopan, we suggest a potentiometric method with our Ag^+-selective membrane electrode. The results obtained compare well with those obtained by using a commercial Br^--selective membrane electrode (Radelkis, OP-Br-7111D) (see Table 6).

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POLAROGRAPHIC DETERMINATION OF AMPICILLIN IN CAPSULES AND TABLETS

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Summary—A new polarographic method is used for quantitative analysis of ampicillin dosage forms. The electroactive product is formed by acidic hydrolysis of ampicillin. It gives a well-developed reduction wave with half-wave potential of −0.91 V *vs.* SCE. The proposed method has good precision. A major advantage is the selectivity, which makes the determination of ampicillin possible without prior separation of the excipient.

Several methods have been described for the determination of ampicillin in aqueous solution, based on ultraviolet spectrophotometry,[1] reaction with iodine,[2] colour formation with hydroxamic acids[3] and reaction with ammonium vanadate.[4] Fluorometric assay of ampicillin in biological fluids has been extensively investigated by several authors.[5–7]

The present paper describes a new polarographic method for ampicillin in tablets and capsules; prior separation of excipient is not necessary in this method.

EXPERIMENTAL

Drugs

Ampicillin (100% chromatographically pure, 86.8% activity) was obtained as the pure compound from Beecham Research Laboratories, England. Standard solutions were prepared, covering a concentration range of 2–3 mg/ml.

Penbritin capsules and Tolomol tablets were obtained from Saval Laboratories and Bayer Laboratories respectively.

For recovery studies, capsule formulations were prepared according to the manufacturer's specifications for 250-mg ampicillin dosages.

Citrate buffer, pH 5.0

Citric acid (42 g) was dissolved in 204 ml of 2*M* sodium hydroxide and the mixture diluted to a litre. Then 990 ml of buffer were mixed with 10 ml of formaldehyde to give 1% concentration of the latter.

Sample preparation

A 10-ml portion of aqueous solution containing between 200 and 300 mg of ampicillin was pipetted into a 100-ml standard flask containing 5 ml of 1*M* sodium hydroxide; 10 min later 5 ml of 1*M* hydrochloric acid were added, followed by dilution to volume with pH 5.0 citrate buffer containing 1% of formaldehyde.

All samples (capsules and tablets) were treated in the same way as the standards. Standard and sample solutions were heated at 100° for 30 min, allowed to cool and then analysed polarographically.

Polarographic analysis

Polarograms were recorded with a three-electrode polarograph (Tacussel assembly) employing a three-compartment polarographic cell. A saturated calomel reference electrode (SCE) and platinum-wire counter-electrode were used. The dropping mercury electrode (DME) had an $m^{2/3}t^{1/6}$ value of 2.70 (m in mg/sec, t in sec). At −1.00 V *vs.* SCE in nitrogen-saturated solution, the current range was 25–50 μA for full-scale deflection on the recorder. The potential was scanned between −0.75 and −1.10 V *vs.* SCE at 2 mV/sec. All solutions were purged with oxygen-free nitrogen for 10 min and polarographed at 25°; no maximum-suppression was needed.

RESULTS AND DISCUSSION

When ampicillin is heated in acid (or alkaline) solution, a strongly fluorescent yellow product is formed, which gives a polarographic reduction wave with half-wave potential of −0.91 V *vs.* SCE. The product has been suggested[8,9] to be a 2,5-diketopiperazine derivative formed by an intramolecular nucleophilic attack on the α-amino group in the side-chain of ampicillin. The polarographic wave can be used for analytical purposes, the current being linearly related to the concentration, the equation being

$$i(\mu A) = 6.57C\,(\text{mg/ml}) + 8.65.$$

Table 1. Results of 7 polarographic analyses of ampicillin in tablets and capsules

	Ampicillin content (%) Tablets*	Capsules†
	77.6	87.2
	81.0	90.0
	76.9	89.6
	74.8	91.2
	78.7	89.8
	79.2	88.2
	78.2	90.9
Average	78.1	89.5
Standard deviation	1.9	1.4

* Bayer Laboratories, Chile; 250 mg of ampicillin + 50 mg of excipients.

† Saval Laboratories, Chile; 250 mg of ampicillin + 25 mg of excipients.

A number of commercial tablets and capsules were analysed by this method (Table 1). The relative standard deviations are below 2%. Recovery tests showed a negative bias of 0.1–1.7% (mean 0.6%).

The application of this method to detect excretion of ampicillin in the urine has been tested, and the detection limit found to be 10 μg/ml, adequate if the rate of excretion is high enough. Otherwise pulse polarography (not available in our laboratories) would have to be used.

The excipients tested, magnesium stearate, stearic acid, mannitol, starch, saccharine, colloidal silica and flavours, were found to have no effect on the method.

The clear advantage of the proposed method over others is that no previous separation is needed, either for urine samples or dosage forms.

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HYDRAZINIUM THIOCYANATE AS A REAGENT FOR DETERMINATION OF COPPER

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Summary—Hydrazinium thiocyanate, N_2H_5SCN, has been used for the determination of copper in copper salts. The reagent reduces the copper ions to the cuprous state and precipitates cuprous thiocyanate $Cu_2(SCN)_2$, quantitatively.

Recently, we reported[1] a novel method for the preparation of hydrazinium derivatives by the reaction of solid ammonium salts with hydrazine hydrate. The hydrazine content of these hydrazinium compounds was determined by titration with potassium iodate. However, it was not possible to determine the hydrazine content of N_2H_5I and N_2H_5SCN since both I^- and SCN^- also react with iodate, so we had to use other methods. During the course of determination of thiocyanate in N_2H_5SCN as $Cu_2(SCN)_2$, we found that reduction of Cu^{2+} to Cu^+ was achieved simultaneously. In the conventional method, Cu^{2+} is usually reduced to Cu^+ by the addition of sulphurous acid,[2] ammonium hydrogen sulphite,[3] ascorbic acid,[4] or ferrous sulphate.[5] It was thought interesting to try to use hydrazinium thiocyanate as a reagent for the determination of copper in copper salts. In this communication we report the results of this investigation.

EXPERIMENTAL

Preparation of hydrazinium thiocyanate

Stoichiometric quantities of ammonium thiocyanate and hydrazine hydrate were mixed. The ammonium salt dissolved instantaneously with evolution of ammonia. The resulting solution was kept over phosphorus pentoxide in a vacuum desiccator for a few days; crystals of N_2H_5SCN were obtained.

$$NH_4SCN + N_2H_4H_2O \rightarrow N_2H_5SCN + NH_3 + H_2O$$

A 10% solution of hydrazinium thiocyanate was used. Copper solutions were prepared by dissolving known amounts of copper metal in nitric acid. Experiments were also carried out with different copper salts such as the chloride, nitrate and sulphate.

Procedure

A copper solution containing up to 0.3 g of copper is diluted to 150–200 ml in a 400-ml beaker. A 10% solution of hydrazinium thiocyanate is then added slowly with constant stirring. The solution becomes colourless, a white precipitate forms, and the supernatant liquid becomes acidic. The precipitate is digested on a water-bath for about an hour, then filtered off on a porosity-3 sintered-glass crucible. The precipitate is washed with cold distilled water and finally with alcohol. The precipitate is dried to constant weight at 110–120° and weighed as $Cu_2(SCN)_2$.

Fe^{3+}, Mn^{2+} and Cr^{3+} do not interfere, but Ag^+ and Hg^{2+} do.

RESULTS AND DISCUSSION

The results for determination of copper in solutions containing different amounts (50–350 mg) of it are given in Table 1. The results show good agreement. The reaction of hydrazinium thiocyanate, N_2H_5SCN, with Cu^{2+} can be written as follows:

$$4Cu^{2+} + 4N_2H_5SCN \rightarrow 2Cu_2(SCN)_2 + 3N_2H_5^+ + 5H^+ + N_2$$

The stoichiometry of the reaction was checked by determination of the hydrazine content in the filtrate after the separation of $Cu_2(SCN)_2$. The liberation of protons accounts for the observed decrease in pH to ~2.0.

This method of determination of copper is convenient, because the reduction to cuprous ions and the precipitation of cuprous thiocyanate are achieved by a single reagent. Also, the time required for the determination is much less than for conventional

Table 1. Results of gravimetric determination of copper

Copper taken, *g*	Copper found, *g*	Error, (%)
0.0536	0.0535	−0.2
0.0717	0.0715	−0.3
0.0770	0.0769	−0.1
0.1044	0.1045	+0.1
0.1305	0.1300	−0.4
0.1750	0.1754	+0.2
0.1991	0.1984	−0.4
0.3368	0.3381	+0.4

Relative standard deviation 0.13%.

methods.[1–5] It is interesting to note that cuprous thiocyanate is not precipitated by addition of hydrazine hydrate and thiocyanate to solutions containing Cu^{2+} ions. Hydrazine hydrate is known[6] to reduce Cu^{2+} to Cu^{+} which either forms Cu_2O or is further reduced to metallic copper.

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A POLAROGRAPHIC CELL SYSTEM WITH A NOVEL TEMPERATURE-CONTROLLED REFERENCE ELECTRODE FOR THE DETERMINATION OF KINETIC PARAMETERS OF ELECTRODE REACTIONS

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Summary—An improved experimental arrangement for the determination of kinetic data relating to polarographic reductions is described. The significant feature is the constant-temperature reference electrode; its construction and use in this context are described. A comparison is made of the more realistic results obtained by these means, with those obtained with a more conventional cell where the temperature of the reference electrode is varied with that of the working solution.

When activation energies of electrode processes are to be determined, it is necessary to measure the appropriate electrode potentials over a range of temperatures. In the case of polarographic reductions, half-wave potentials have to be determined over a considerable temperature range. When doing this it is of prime importance to take account of the temperature coefficient of the potential of the reference electrode, which for polarographic purposes is usually the saturated calomel electrode.

Despite great improvements in the preparation and design of the calomel electrode, as suggested by Ives and Janz,[1] and despite its improved reproducibility at 298 K, it has been shown to exhibit unfortunate hysteresis effects at elevated temperatures.[1-3] Wingfield and Acree[4] estimated temperature hysteresis effects to be as high as 0.5–0.9 mV and found that maximum potential changes occurred over a period of 2–3 hr for an 8° change in temperature.

For small temperature variations the potential of the saturated calomel electrode may be represented by

$$E' = 0.2444 - 0.0025\,(t - 25)$$

with t in °C, but at higher temperatures the following relationship applies:

$$E'' = 0.2412 - 6.61 \times 10^{-4}\,(t - 25) - 1.75 \times 10^{-6}t - 25)^2 - 9.00 \times 10^{-10}\,(t - 25)^3$$

where

$$E' = E_{\text{calomel}} + E_{\text{liquid junction}} \quad \text{and}$$
$$E'' = E_{\text{calomel}}.$$

Temperature hysteresis has evidently interfered seriously with the determination of the temperature coefficient of the calomel electrode. Thus Wingfield and Acree estimated the temperature coefficient to be -0.25 mV/deg which is in fair agreement with the value of -0.20 mV/deg obtained by Ewing[5] and -0.22 mV/deg reported by Bjerrum and Unmack,[6] but differs markedly from the value of -0.7 mV/deg quoted by Findlay.[7]

Unless appropriate precautions are taken, these variations are carried over to attempted determinations of half-wave potentials. Not only will uncertainty be introduced into the measured values of $E_{1/2}$ but, more seriously, the *slopes* of the polarographic waves may vary in a non-reproducible manner and yield unreliable estimates of transfer coefficients. Reliable values of αn for an electrochemical process are a prime prerequisite for the calculation of kinetic data.

The authors have found that more realistic results may be obtained by using a separate thermostatically-controlled calomel electrode of suitable design, which is maintained during its life at a temperature of 298 K. The complete cell system is shown schematically in Fig. 1. The "H-cell" contains in limb A the working solution, dropping electrode and nitrogen degassing lines. Agar plug B, separated by sintered disc C, provides electrical contact with the saturated

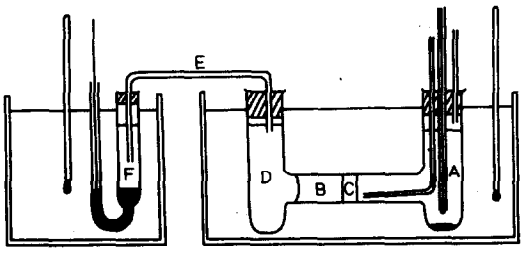

Fig. 1. Schematic representation of cell components (see text).

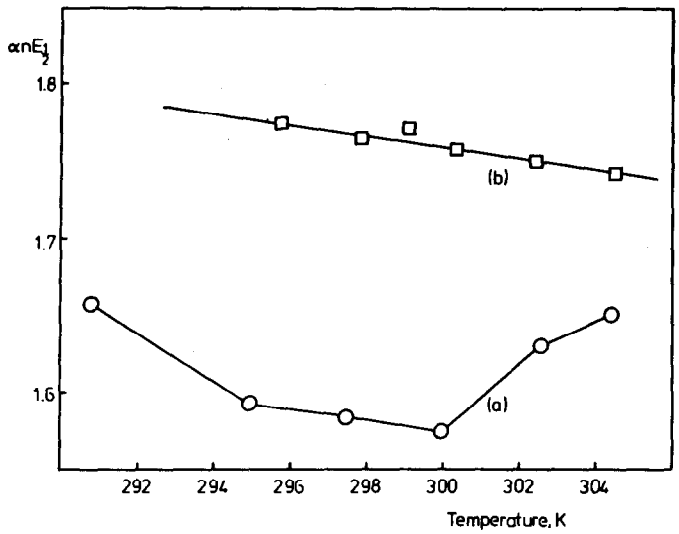

Fig. 2. Variation of the quantity $\alpha n E_{1/2}$ with temperature for the aquo-Zn^{2+} system. $[Zn^{2+}] = 5 \times 10^{-4} M$; [KCl] = 0.1 M Curve *a*—temperature of calomel electrode varied. Curve *b*—temperature of calomel electrode maintained at 298 K.

solution of supporting electrolyte in limb D. This cell is contained in a water-bath controlled at a preselected temperature, *e.g.*, by a "Circon" unit, to within ±0.1°. A KCl/agar salt-bridge, E, provides electrical contact between the limb D and the saturated calomel electrode F, immersed in a separate water-bath maintained at 25 ± 0.1° by a second "Circon" or similar unit.

The design and construction of the calomel electrode follows the basic stipulations of Ives and Janz:[1] the geometry of the electrode compartment, requiring a low ratio of mercury area to solution volume, as suggested by Covington *et al.*, takes the form of an elongated hydrophobically-treated glass tube. The thoroughly cleaned and dried tube is heated to 60° and filled with a 1% solution of Dow-Corning Silicone Fluid No. 200 in carbon tetrachloride. After draining, and heating for 2 hr at 165°, the tube is

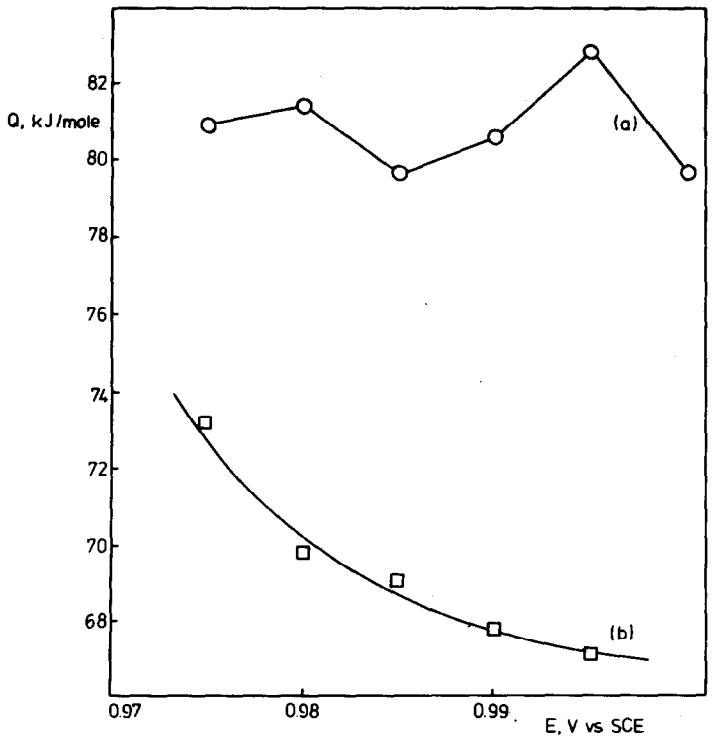

Fig. 3. Variation of electroreduction activation energy, Q, of the Zn^{2+} aquo-ion. Curve *a*—temperature of calomel electrode varied. Curve *b*—temperature of calomel electrode maintained at 298 K.

rinsed several times with carbon tetrachloride to remove unbonded silicones, after which it is ready for use. The adverse effect of such treatment upon platinum–glass seals makes it necessary to avoid using these for making electrical contacts.

Improvements brought about by taking these precautions are shown by a comparison of the temperature variation of the quantity $\alpha n E_{1/2}$ (α = transfer coefficient, n = number of electrons exchanged, $E_{1/2}$ = half-wave potential) and of the finally determined activation energy, Q, for the aquo-zinc system shown in Figs. 2 and 3. Experimental results obtained with the apparatus described here show the regular trends to be expected, while those obtained with a system in which both the reference and indicator electrodes were subjected to variable temperature show erratic variations. Activation energies were calculated as described earlier.[8]

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COLORIMETRIC DETERMINATION OF SOME SULPHONAMIDES WITH PHENOTHIAZINE

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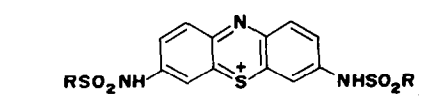
Summary—Two simple and sensitive colorimetric procedures for determination of some sulphonamides with phenothiazine (thiodiphenylamine) are presented. One is based on reaction in aqueous alcohol solution in presence of hypochlorite, with direct measurement at 515 nm. The other is based on reaction in presence of copper(II) acetate at 70°, extraction with chloroform and measurement at 515 nm. The method is applied to the determination of sulphonamides in pure and tablet form, with a coefficient of variation less than 2%.

Various methods have been reported for the determination of sulphonamides. These include diazometric,[1–3] bromometric,[4–6] non-aqueous titrimetric,[7–9] complexometric,[10–13] argentimetric,[14] ultraviolet and infrared spectrophotometric,[15–20] polarographic,[21,22] and chromatographic[23–25] methods. Colorimetric methods have been based on diazotization and coupling with phenols or arylamines[26] such as *N*-(1-naphthyl)ethylenediamine (Bratton and Marshall reagent),[27] *N*,*N*-diethyl-*N*-(1-naphthyl)ethylenediamine oxalate,[28] α-naphthylamine,[29] thymol[30] and resorcinol,[31] and also on reaction with 1,2-naphthoquinone-4-sulphonate,[32] chromotropic acid,[33] 9-chloroacridine[34] and *o*-diacetylbenzene,[35] or through formation of Schiff bases with *p*-dimethylaminobenzaldehyde,[36,37] 4-dimethylaminocinnamaldehyde[38] and salicylaldehyde.[39]

Feigl and Haguenauer-Castro[40–42] used phenothiazine (thiodiphenylamine) as a chromogenic reagent to detect chloramine-T (sodium *N*-chloro-*p*-toluenesulphonamide) and other *N*-halosulphonamides by the production of a red violet thiazine dye-stuff soluble in ether, benzene, chloroform or carbon disulphide. The chemistry of these colour reactions is not known with certainty because the coloured product has not been isolated in pure form. Feigl and Haguenauer-Castro[40–42] suggested that the toluene-



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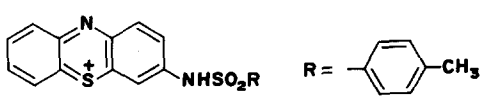

II

p-sulphonamide and sodium hypochlorite produced by the hydrolysis of chloramine-T undergo oxidative condensation with phenothiazine to produce a red-violet thiazine dyestuff, with formula **I** or **II**. Primary arylamines such as aniline and *p*-aminobenzoic acid have been tested and found to give colours ranging from green to blue when reacted with phenothiazine under these conditions. Accordingly, we suggest the use of phenothiazine in presence of hypochlorite solution as a reagent for the colorimetric determination of compounds containing the $-SO_2NH$ group, sulphonamides in particular.

Recently Tanaka *et al.*[43] described a procedure for the determination of saccharine in soft drinks by use of phenothiazine and copper(II) acetate, but did not discuss the nature of the product or the reaction. However, the product is presumably similar to that in the Feigl reaction, *i.e.*, reaction of the phenothiazine with the sulphonamide is promoted by the oxidizing power of the Cu^{2+} ion, the role of Cu^{2+} and OCl^- in the two reactions probably being similar. This point is now under investigation in our laboratory.

Here we use both reactions for the colorimetric determination of some sulphonamides with phenothiazine.

EXPERIMENTAL

Reagents

Phenothiazine solution. Dissolve 0.5 g of phenthiazine, previously recrystallized twice from alcohol (m.p. 186°), in 100 ml of ethanol. Prepare fresh daily.

Hypochlorite solution. Shake 5 g of bleaching powder (30% w/w available chlorine) with 100 ml of distilled water for 1 min, leave to settle and filter. Add to the filtrate 3 ml of 10% sodium hydroxide solution and filter. Prepare fresh daily.

Copper(II) acetate solution. A 0.5% solution in 0.5% acetic acid.

Sulphonamide solutions. Dissolve, warming if necessary, 80 mg of sulphonamide in ethanol and dilute to 100 ml with ethanol. Dilute 10 ml to 100 ml with 50% aqueous ethanol.

Procedure A

Transfer a 5-ml portion of sulphonamide solution into

Table 1. Analytical data for phenothiazine colour reaction with sulphonamides by the two procedures

Compounds	Procedure A range, mg/25 ml	c.v., %*	ε†	Procedure B range, mg/25 ml	c.v., %*	ε†
Sulphadiazine	0.2–1.0	±0.4	7.16×10^3	0.1–0.5	±1.07%	1.02×10^4
Sulphadimidine	0.1–0.8	±0.4	8.09×10^3	0.1–0.6	±0.85%	9.40×10^3
Sulphathiazole	0.1–0.5	±0.3	7.41×10^3	0.1–0.5	±1.95%	9.80×10^3
Sulphamerazine	0.1–0.6	±0.6	7.65×10^3	0.2–0.6	±1.07%	1.00×10^4
Sulphadimethoxine	0.1–0.5	±0.5%	5.54×10^3	0.2–0.9	±1.40%	5.74×10^3
Sulphasomidine	0.2–1.0	±0.6%	3.56×10^3	0.2–1.0	±1.15%	4.64×10^3
Sulfisoxazole	0.2–0.8	±0.4%	4.28×10^3	0.2–1.0	±0.67%	5.16×10^3
Sulphaguanidine	0.2–0.8	±1.1%	6.74×10^3	0.1–0.5	±1.40%	6.03×10^3

* 6 separate determinations.
† $\epsilon = (A \times \text{m.w. of sulphonamide})/10 \times$ sulphonamide concentration (% w/v).

a 25-ml standard flask. Add 1 ml of phenothiazine solution, 5 ml of ethanol, 1 ml of 3.5% acetic acid, and 1 ml of hypochlorite solution. Mix, and dilute to volume with ethanol. Measure the absorbance, in 1-cm cells, at 515 nm, against a blank prepared by applying the procedure to 5 ml of 50% aqueous ethanol. Calculate the concentration of the sulphonamide from a calibration graph prepared with standard solutions.

Procedure B

Transfer a 5-ml portion of sulphonamide solution into a test-tube. Add 1 ml of copper acetate solution, 1 ml of phenothiazine solution, and 2 ml of ethanol. Heat in a water-bath at 65–70° for 1 hr. Cool to room temperature and transfer—including any precipitate—to a separating funnel with 2 ml of ethanol and 60 ml of distilled water. Extract successively with 10-, 5-, and 5-ml portions of chloroform, shaking each time for 1 min. Collect the extracts in a 25-ml standard flask and make up to volume with chloroform. Measure the absorbance, in 1-cm cells, at 515 nm, against a blank prepared by applying the procedure to 5 ml of 50% aqueous ethanol. Calculate the concentration of the sulphonamide from a calibration graph prepared with standards.

Procedure for tablets

Take an accurately weighed amount of the powdered tablets equivalent to about 80 mg of sulphonamide. Extract with hot ethanol. Filter and make up to the mark in a 100-ml standard flask. Dilute 10 ml to 100 ml with 50% v/v ethanol. Apply procedure A or B to 5-ml of this solution.

Table 2. Results obtained by the proposed methods and by the B.P. method

Sulphonamides in pure form and in tablets*	Recovery, %† Procedure A	Procedure B	B.P. 1973
Sulphadiazine			
Powder	100.0 ± 0.3	100.0 ± 1.1	100.0 ± 0.2
Tablets	100.1 ± 0.9	100.7 ± 1.0	99.7 ± 0.5
Sulphadimidine			
Powder	100.0 ± 0.4	100.0 ± 0.9	99.9 ± 0.5
Tablets§	99.4 ± 1.5	100.4 ± 0.6	—
Sulphathiazole			
Powder	100.0 ± 0.3	100.0 ± 1.9	100.3 ± 0.4
Tablets§	99.6 ± 0.7	100.1 ± 0.9	—
Sulphamerazine			
Powder	100.0 ± 0.6	100.0 ± 1.1	99.9 ± 0.6
Tablets§	100.1 ± 0.8	100.0 ± 0.6	—
Sulphadimethoxine			
Powder	100.0 ± 0.5	100.0 ± 1.4	100.3 ± 0.1
Tablets	100.8 ± 0.8	100.3 ± 0.7	100.2 ± 1.1
Sulphasomidine			
Powder	100.0 ± 0.6	100.0 ± 1.2	100.0 ± 0.6
Tablets	100.3 ± 1.0	99.9 ± 1.1	100.0 ± 0.5
Sulfisoxazole			
Powder	100.0 ± 0.4	100.0 ± 0.7	100.0 ± 0.5
Tablets	99.9 ± 1.6	100.7 ± 1.0	99.8 ± 0.9
Sulphaguanidine			
Powder	100.0 ± 1.1	100.0 ± 1.4	99.8 ± 0.4
Tablets	99.9 ± 1.2	99.7 ± 0.8	99.6 ± 0.7

* Tablets contain 500 mg in each.
† Average of 6 experiments, recovery from the nominal or added sulphonamide content.
§ Tablets prepared in laboratory with lactose, starch, talc and magnesium stearate as tablet fillers..

RESULTS AND DISCUSSION

Eight sulphonamides, namely sulphadiazine, sulphadimidine, sulphathiazole, sulphamerazine, sulphadimethoxine, sulphasomidine, sulfisoxazole, and sulphaguanidine were found to react with phenothiazine to give a red colour.

A study of the effect of the concentrations of the different reagents in both procedures, with respect to maximum sensitivity, minimum blank and obedience to Beer's law, led to procedures A and B above.

The red colour produced in both procedures under the conditions described was found to be stable for 3 hr and to obey Beer's law over the concentration ranges given in Table 1. The correlation coefficients were between 0.9993 and 0.9999. Several runs at different concentration levels of each drug gave a coefficient of variation less than 2%. The apparent molar absorptivity, ϵ, obtained for each drug by both procedures showed that the two methods had similar sensitivity (Table 1).

Phenothiazine solution in ethanol is yellow but under the conditions of procedure A it becomes slightly red after addition of the hypochlorite. This could be due to an oxidation intermediate which subsequently enters the reaction with the sulphonamide. The absorbance of the blank solution in procedure A, measured the solvent medium (50% aqueous ethanol) at 515 nm was found to be about 0.335. The blank solution of procedure B has a negligible absorbance when measured against chloroform at 515 nm.

Procedure A has the advantage of being rapid, but procedure B can be recommended when the other ingredients are known to be insoluble in chloroform but to interfere with the measurements in aqueous media. Procedures A and B have been applied to the determination of the above-mentioned sulphonamides in pure form and in tablets. The results obtained (Table 2) are both precise and accurate. The possibility of interfering constituents in tablets cannot be overlooked. Therefore, both procedures were compared with the official B.P. method whenever the true content per tablet was unknown. Comparable results were obtained (Table 2).

An advantage over the Bratton and Marshall method is that the absorbance is stable for 3 hr. In the former method, absorbance readings must be made within 15 min of colour development, because of precipitation of the azo dyes formed.[44]

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DETERMINATION OF THIOUREA AND SOME OF ITS ORGANIC DERIVATIVES WITH SODIUM VANADATE, HEXACYANOFERRATE(III), CERIUM(IV) SULPHATE, MANGANESE(III) AND MANGANESE(IV)

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Summary—The determination of thiourea and some of its organic derivatives with sodium vanadate, hexacyanoferrate(III), cerium(IV) sulphate, manganese(III) and manganese(IV) is described. A mixture of iodate and iodide is used as catalyst. Ferroin, *N*-phenylanthranilic acid and *p*-ethoxychrysoidine can be used as indicators.

Thiourea possesses several industrial, medicinal and analytical applications, and consequently its determination has received considerable attention. The various methods used are based on its tendency to react with metals either to undergo desulphurization or complex formation, or on its quantitative oxidation to different products by various oxidants in acidic and alkaline media. They were reviewed by Gupta[1] and Singh and Verma.[2] The other methods were recently well documented by Cyganski.[3] The present work describes the determination of thiourea and some organic derivatives *viz*., *N*-phenyl thiourea, *N*,*N*′-diethyl thiourea and *N*,*N*′-diphenyl thiourea with sodium vanadate, hexacyanoferrate(III), cerium (IV) sulphate, manganese(III) and manganese(IV) by simple and direct titrimetric methods in presence of a mixture of iodate and iodide (as catalyst), with ferroin, *N*-phenylanthranilic acid or *p*-ethoxychrysoidine as indicator.

EXPERIMENTAL

Reagents

Thiourea and *N*,*N*′-diethyl thiourea: 0.1*M* solutions were prepared in distilled water and standardized.[2,4]

N-Phenyl thiourea and *N*,*N*′-diphenyl thiourea: 0.1*M* solutions were prepared in 50% v/v sulphuric acid and standardized with potassium iodate.[5]

Solutions (0.1*M* of cerium(IV) sulphate,[4] potassium hexacyanoferrate(III),[6] sodium vanadate[4] and manganese(III)[6,7] and a 0.05*M* solution of manganese(IV)[8] were prepared and standardized.

Catalyst solution was prepared by mixing 20 ml of 0.1*M* potassium iodide and 4 ml of 0.1*M* potassium iodate and diluting to 250 ml.

Ferroin (0.025*M*), 0.1% *N*-phenylanthranilic acid and 0.1% *p*-ethoxychrysoidine solutions were prepared in distilled water.[4] All other reagents used were of analytical reagent grade.

Procedure

Enough 10*M* sulphuric acid is added to the sample to give 6*M* acid concentration after titration with sodium vanadate, hexacyanoferrate(III) or cerium(IV) sulphate, or 4*M* after titration with manganese(III) or manganese(IV), in a total volume of 100 ml. Then 5 ml of catalyst mixture are added, followed by dilution with distilled water so that the total volume at the equivalence point will be 100 ml. The solution is then titrated with the standardized oxidant, with 0.05 ml of ferroin or 0.2 ml of *N*-phenylanthranilic acid or *p*-ethoxychrysoidine solution as indicator.

RESULTS AND DISCUSSION

The difficulties encountered in the determination of thiourea and its organic derivatives with cerium(IV) sulphate, potassium hexacyanoferrate(III) and manganese(III) are widely discussed.[1,2] Sodium vanadate and manganese(IV) have not previously been used for the direct determination of thiourea or its organic derivatives. We have now used all five titrants for the purpose, in sulphuric acid medium with a mixture of iodate and iodide as catalyst. The acid and the catalyst concentration ranges for a total volume of 100 ml are given in Table 1. At concentrations of acid and catalyst below those given in the table, the reaction with sodium vanadate or hexacyanoferrate(III) is slow, and with the other oxidants the reaction proceeds beyond the disulphide stage. At acid concentrations above those proposed, the reaction with cerium(IV) sulphate is slow, and with the other oxidants the reaction proceeds beyond the disulphide stage because the reaction between the catalyst and the reductant is slow. Larger volumes of the catalyst have no adverse effect, but small volumes are always preferable because the brown colour of larger amounts of iodine masks the colour change of the indicator.

In the titration with hexacyanoferrate(III) a white precipitate is formed at sulphuric acid concentrations above 4*M*, and increases as the titration progresses.

Table 1. Conditions for the determination of thiourea and some of its organic derivatives

Species titrated	Titrant	0.1*N* solns. Acid, *M*	0.1*N* solns. Catalyst, *ml*	0.01*N* solns. Acid, *M*	0.01*N* solns. Catalyst, *ml*
Thiourea	Sodium vanadate	5–8	1.0–6.0	5–8	1.0–4.0
	Hexacyanoferrate(III)	5–8	0.6–5.0	—	—
	Cerium(IV) sulphate	4–8	0.2–6.0	4–8	0.2–4.0
	Manganese(III)	3–6	2.0–6.0	—	—
	Manganese(IV)	2–4	4.0–6.0	—	—
N-Phenyl thiourea	Sodium vanadate	5–8	1.0–6.0	5–8	1.0–6.0
	Hexacyanoferrate(III)	5–7	2.0–5.0	—	—
	Cerium(IV) sulphate	5–8	0.6–6.0	5–8	0.6–6.0
	Manganese(III)	3–5	5.0–6.0	—	—
	Manganese(IV)	3–5	5.0–6.0	—	—
N,N'-Diethyl thiourea	Sodium vanadate	5–8	2.0–6.0	5–8	1.0–4.0
	Hexacyanoferrate(III)	5–8	1.0–5.0	5–8	1.0–4.0
	Cerium(IV) sulphate	5–8	2.5–5.0	5–8	2.0–4.0
	Manganese(III)	3–6	4.0–6.0	—	—
N,N'-Diphenyl thiourea	Sodium vanadate	6–7	0.5–5.0	5–7	0.5–3.0
	Hexacyanoferrate(III)	6–7	2.0–5.0	5–8	1.5–4.0
	Cerium(IV) sulphate	6–8	2.5–5.0	5–8	1.0–4.0

It is ferrocyanic acid, as pointed out by Bates *et al.*,[9] and confirmed by qualitative tests.

The iodine produced by the acid and the catalyst mixture first oxidizes the thiourea or its derivatives to the disulphide, itself being reduced to iodide and re-oxidized by the titrant. At the end-point, when all the iodide has been converted into iodine, the first excess of titrant reacts with the indicator.

With ferroin as indicator, its normal colour deepens and there is a brownish red precipitate just before the equivalence point. This is possibly due to the formation of the $Fe(phen)_3^{2+}$–$2I_3^-$ complex, as pointed out by Gopala Rao *et al.*[10] The colour change from brownish red precipitate to pale blue is sharp and the precipitate disappears. The colour change is from pink to yellow with *p*-ethoxychrysoidine and from yellow to violet with *N*-phenylanthranilic acid. Ferroin and *p*-ethoxychrysoidine can be added at the beginning but *N*-phenylanthranilic acid acid should preferably be added near the equivalence point, when the colour of iodine starts to appear, since the indicator is partially destroyed if added at the beginning. With hexacyanoferrate(III), only ferroin is satisfactory as indicator. The indicator correction is negligible. The ranges of determination and coefficients of variation are given in Table 2.

Quantitative results are not obtained in the titration of *N,N'*-diphenylthiourea with manganese(III) and of *N,N'*-diethylthiourea and of *N,N'*-diphenylthiourea with manganese(IV). High values are obtained when more than 0.6 mmole of thiourea or its derivatives is titrated with manganese(III) or manganese(IV).

The titrations can also be done with 0.01*N* solutions. Accurate results are obtained with sodium vanadate, hexacyanoferrate(III) and cerium(IV) sulphate, but low results are obtained with manganese (III) and manganese(IV). The acid and catalyst concentrations are given in Table 1. The indicator correction is found to be 0.2 ml with 0.01*N* oxidant solutions. The maximum relative error with respect to methods used for standardization ranged from 0.35 to 0.85%.

Sastry[11] has reported that the conditional hexa-

Table 2. Determination of thiourea and some of its organic derivatives

Substance determined	Range of the substance determined, *mg* Sodium vanadate	Hexacyano-ferrate(III)	Cerium(IV) sulphate	Manganese (III)	Manganese (IV)
Thiourea	37–150 (0.2)	37–150 (0.2)	37–150 (0.2)	15–37 (0.3)	15–37 (0.3)
N-Phenyl thiourea	70–280 (0.2)	70–280 (0.2)	70–280 (0.2)	28–70 (0.3)	28–70 (0.3)
N,N'-Diethyl thiourea	65–264 (0.2)	65–264 (0.2)	65–264 (0.2)	26–66 (0.4)	
N,N'-Diphenyl thiourea	41–416 (0.2)	41–416 (0.2)	41–416 (0.2)		

The values given in parentheses represent the maximum coefficient of variation (4 determinations).

cyanoferrate(III)/(II) potential increases from 0.675 V in 0.48*M* sulphuric acid to 1.357 V in the 6.65*M* acid. Hence at the acidity used, hexacyanoferrate(III) can oxidize ferroin.

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THE DETERMINATION OF LEAD IN 13 USGS STANDARD ROCKS*

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Summary—Lead was determined in 13 U.S. Geological Survey standard rocks by graphite furnace atomization and atomic-absorption spectrometry after extraction of lead with diethylammonium diethyldithiocarbamic acid. An analysis of variance of the results obtained from a random sampling of three different bottles of each standard rock showed no heterogeneity among bottles, at the $F_{0.95}$ level, for a 100-mg sample-size. The relative error of the method, based on the standard deviation of the mean within bottles, was generally less than 10%.

The electrothermal atomic-absorption technique has proved to be a very sensitive method for detecting small amounts of metals in a variety of materials. General reviews of the method have been given in the literature.[1,2] The determination of lead by this technique, however, has been shown to be rather prone to interference, *e.g.*, from Ca, S, Al, Na, K, Sr, Mg and Ba.[3–8] Although ways have been proposed for reducing or eliminating some of these problems, we felt that a quick separation of the major interfering elements would give more reliable results for a larger variety of samples. Lead has been separated from rocks and minerals previously by diethylammonium diethyldithiocarbamate extraction.[9,10] The effectiveness of the separation was tested by analysis of a variety of rock samples of known lead content. Additionally, an analysis of variance was made on three determinations from three different splits (bottles) of each standard rock to determine the degree of homogeneity among various bottles of the same rock standard.

EXPERIMENTAL

Reagents

Lead standard solution (1.000 mg/ml). Dissolve 399.6 mg of $Pb(NO_3)_2$ in a 250-ml standard flask with 2% nitric acid. Prepare a 10-ppm lead standard by 100-fold dilution of the solution with 5% hydrochloric acid.

Ascorbic acid solution 2%.

Diethylammonium diethyldithiocarbamate 0.25%. Dissolve 0.50 g of the salt in 200 ml of xylene. Prepare fresh daily.

Apparatus

Atomic-absorption spectrophotometer. A Perkin–Elmer model 503 atomic-absorption spectrophotometer equipped with a model HGA-2100 graphite furnace, model 56 recorder, and deuterium background-correction was used for all measurements. The settings used were: wavelength 283.3 nm, dry at 110° for 20 sec, char at 550° for 20 sec, atomize at 2600° for 8 sec, argon flow 30 ml/min, non-pyrolitic graphite tubes.

Solvent extraction apparatus. Extractions were made by mixing the phases in the separatory funnel with a stream of compressed air.[11] Eighteen 1-mm bore glass capillary tubes were connected with Tygon tubing to a stainless-steel pipe in series with a compressed air supply and inserted into the eighteen separatory funnels, and the extraction was performed by mixing of the two layers with air bubbles.

Procedure

Transfer a 100-mg sample to a Teflon beaker and add 2 ml of conc. perchloric acid, 5 ml of conc. nitric acid and 10 ml of conc. hydrofluoric acid. Evaporate to dryness on a hot-plate at 200°. Dissolve the residue with 10 ml of 10% hydrochloric acid with gentle heating for several minutes. Transfer the solution to a thoroughly cleaned 60-ml separatory funnel and add 5 ml of 5% ascorbic acid solution. Mix for 1 min, using the bubbler-extraction apparatus. Add 10 ml of 0.25% DDTC solution in xylene and extract for 5 min with the bubbler apparatus. Drain and discard the aqueous layer. Rinse the funnel wall with approximately 5 ml of water, drain and discard the aqueous phase. Repeat this rinsing step. Add 10 ml of 30% nitric acid and extract with the bubbler apparatus for 10 min. Drain the lower layer into a 25-ml standard flask, rinse the funnel with several ml of water, adding the rinsings to the solution in the flask, and make up to volume. Determine the lead content by atomic absorption with a 20-μl aliquot, and comparing the peak height with those for standard solutions of lead (1.0–6.0 μg Pb) treated in the same way.

RESULTS AND DISCUSSION

DDTC was chosen for the separation of lead because the extraction can be performed in fairly acid solutions, thus eliminating the need to control the pH precisely, as required in the dithizone methods, and at the same time should provide a certain amount of separation from other elements.[12] The yield was

* Publication authorized by The Director, U.S. Geological Survey.

Table 1. Lead in 13 USGS standard rocks (σ, standard deviation within-bottles NS = not significant at $F_{0.95}$)

Standard rock	Description	Bottle (split/position)	Lead, *ppm*	Mean ± σ, *ppm*	Relative error, (%)	*F*
AGV-1	Andesite	10/24 38/1 56/14	35.8, 34.3, 38.3 34.8, 36.3, 39.3 37.8, 37.8, 34.3	36.5 ± 2.1	5.8	0.08 NS
BCR-1	Basalt	5/32 75/6 47/1	15.0, 13.8, 13.5 13.3, 14.5, 13.8 14.3, 13.3, 15.3	14.1 ± 0.8	5.8	0.21 NS
BHVO-1	Basalt	62/20 10/7 31/13	2.3, 2.0, 2.3 2.8, 2.8, 2.8 2.8, 2.0, 2.8	2.5 ± 0.3	11.3	3.34 NS
DTS-1	Dunite	6/17 3/9 55/23	6.8, 8.0, 7.5 7.3, 7.5, 8.2 8.5, 7.3, 7.0	7.6 ± 0.6	8.4	0.11 NS
G-2	Granite	3/30 68/4 116/30	29.5, 32.0, 30.0 30.0, 30.5, 29.3 30.5, 31.0, 29.3	30.2 ± 1.0	3.2	0.25 NS
GSP-1	Granodiorite	80/16 38/32 44/29	53.8, 56.7, 57.5 55.0, 56.8, 57.0 56.8, 56.3, 55.5	56.2 ± 1.3	2.4	0.03 NS
MAG-1	Marine mud	38/19 64/11 62/3	26.5, 25.3, 24.5 25.8, 27.5, 24.3 27.2, 25.8, 28.8	26.2 ± 1.4	5.3	1.42 NS
PCC-1	Peridotite	43/4 25/2 19/32	8.0, 8.3, 8.5 8.0, 8.3, 8.5 7.8, 8.3, 8.4	8.2 ± 0.3	3.4	0.13 NS
QLO-1	Quartz latite	51/7 36/30 /31	20.8, 20.8, 20.3 21.8, 21.0, 20.0 22.5, 21.8, 21.3	21.1 ± 0.7	3.1	2.96 NS
RGM-1	Rhyolite	47/25 63/19 19/18	22.3, 24.0, 23.3 24.0, 24.5, 22.5 22.8, 23.2, 23.3	23.3 ± 0.8	3.4	0.44 NS
SCO-1	Cody shale	39/4 46/23 53/29	31.3, 31.0, 29.8 31.3, 31.5, 33.0 30.5, 30.3, 30.5	31.0 ± 0.7	2.3	3.83 NS
SDC-1	Mica schist	115/10 76/13 120/28	23.3, 22.0, 22.0 23.3, 23.8, 23.0 23.8, 22.0, 22.8	22.9 ± 0.7	3.1	1.27 NS
STM-1	Nepheline syenite	57/14 21/1 33/20	17.5, 18.0, 17.0 18.0, 19.3, 17.2 17.3, 17.2, 17.3	17.6 ± 0.7	3.8	1.43 NS

tested with radioactive tracer ^{210}Pb (half-life = 22 y) and found to ≥98%. This high yield was confirmed by the fact that the absorbance of standards to which the whole procedure was applied was within 5% of that of standards measured directly. Ascorbic acid was used to reduce Fe(III), which would otherwise oxidize the reagent and thereby possibly cause low extraction yields. A low concentration of reagent in xylene was used to limit the amount of iron co-extracted with lead.

Although a direct quantitative measurement of the lead in the organic phase can sometimes be made, we found that the lead complex was rather unstable, decomposing in a few hours. In addition, data on spiked samples showed the existence of a suppressive interference which varied from 5% in some samples to more than 30% in others. Solutions obtained by stripping the lead with nitric acid were stable for several days and no interference was observed in any of the samples tested.

The graphite furnace conditions chosen were mainly those recommended by the manufacturer, and variations of 100–200° in the char and atomization temperatures caused no difference in the results. The sensitivity found was 18 pg for 1% absorption, and the calibration was linear up to about 2000 pg. The blank for the entire procedure was 60 ± 12 pg, giving a detection limit (based on three times the variation in the blank) of 0.5 ppm lead in the rock sample. This blank was accomplished only by testing the acids

Table 2. A comparison of the lead content (ppm) with literature values

Standard rock	This method	Literature
AGV-1	36.5 ± 2.1	36.1,[13] 36.53[16]
BCR-1	14.1 ± 0.8	14.3,[13] 13.56[16]
DTS-1	7.6 ± 0.6	9.7[13]
G-2	30.2 ± 1.0	30.5,[13] 30.8[18]
GSP-1	56.2 ± 1.3	56.2,[13] 58.7[19]
PCC-1	8.2 ± 0.3	10.2[13]

used and choosing only those lots which gave an absorbance of ≤ 0.002 for a 20-μl sample. These acid solutions were tested without chemical separation of the lead, because the matrix did not cause major interference with the lead signal. Reagent grade 70% perchloric acid, doubly distilled from a Vycor flask, was used throughout but was not tested directly.

Table 1 gives a list of the individual results on splits from different bottles of each standard rock. A one-way analysis of variance showed that at $F_{0.95}$ there was no significant difference between bottles of any particular standard. Thus within the precision of this method (2.3–11.3% relative error) and the stated confidence limits, the lead content is the same among bottles as within any bottle of a particular standard rock.

Table 2 is a comparison of the mean lead concentrations determined by this method with literature values. The results are generally in good agreement with mass spectrometric and substoichiometric isotope dilution values, differing by less than 5% except for the ultramafic rocks DTS-1 and PCC-1.

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METAL OXIDE REDUCTION: A LOW-TEMPERATURE REACTION WITH GRAPHITE IN FLAMELESS ATOMIC-ABSORPTION SPECTROMETRY

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Summary—The ability of graphite to reduce metal oxides to the free metal is discussed. Differential thermal analysis and X-ray photoelectron spectroscopy are used to investigate the reaction in the case of $CuSO_4$. The reduction process is shown to occur at temperatures which are low relative to the appearance temperature of Cu. These results suggest that the appearance temperature of the element is governed by the vapour pressure of the metal and not by the reduction process.

The processes by which gaseous metal atoms are formed from the desolvated metal salt are an aspect of graphite-furnace atomic-absorption spectroscopy which has received attention over the past few years. At relatively low temperatures, many salts decompose to form the metal oxide. Upon further heating, one mechanism of formation of metal atoms is reduction of the metal oxide with graphite followed by the vaporization of the metal into the gas phase above the atomizer surface. To ascertain the importance of reduction of the metal oxide by graphite, Aggett and Sprott[1] measured the appearance temperatures for various elements, from both a tantalum and a graphite atomizer. From their results, they concluded that for certain elements, such as Co, Fe, Ni and Sn, reduction of the metal oxide by graphite was an important factor in the atomization process. Campbell and Ottaway[2] calculated for 27 elements the temperature at which the standard free energy ΔG° for the reaction of the metal oxide with graphite to yield the metal vapour and carbon monoxide became equal to zero. They found that a good correlation existed between this calculated temperature and the measured appearance temperature for most of the elements studied. More recently, Sturgeon *et al.*[3] were able to distinguish between thermal dissociation of the metal oxide or halide and graphite reduction of the metal oxide, followed by atomization of the metal, as mechanisms of atom formation in graphite furnaces. This was achieved by using early time absorption measurements to determine activation energies for the vaporization or atomization process.

The role of graphite in reducing metal oxides has usually been studied at the appearance temperature of the metal, the vaporization being considered to be simultaneous with the reduction process.[2] In some cases this may actually occur, but in others the reduction of the metal oxide may take place at temperatures several hundred degrees lower than the appearance temperature. In the latter case, the formation of the metal vapour may depend on the temperature of the atomizer and the vapour pressure of the metal. Factors such as heating rates, oscillator strengths and cell geometry may also play a part.

This paper describes the example of a metal oxide which is reduced at temperatures well below that required for vaporization of the free metal from the surface of the atomizer.

EXPERIMENTAL

A Tracor (Model 202) differential thermal analysis (DTA) apparatus, operated at a heating rate of 10°/min, was used for these studies. Samples were mixed for 20 min, by means of a Wig-L-Bug. Platinum sample boats were used to minimize reaction of the boat with the sample. Alumina was used as a reference material and the sample compartment was bathed with nitrogen as a sheath gas.

A Physical Electronics (Model 548) electron spectrometer was used for the ESCA experiments. The graphite filament atomizer[4] and power supply[5] used to prepare the filament atomizer for these experiments have been described previously.

All chemicals were reagents grade with the exception of the graphite powder (200 mesh) which was spectroscopic grade. Solutions were made with triply-distilled water.

RESULTS AND DISCUSSIONS

In any study of metal oxide reduction by graphite at temperatures lower than the appearance temperature of the metal, restrictions must be placed on the choice of the analyte. Thermal decomposition of the metal salt must occur below the upper temperature limit imposed by the DTA apparatus. As the system was continuously flushed with nitrogen, so reducing the partial pressure of carbon monoxide to a negli-

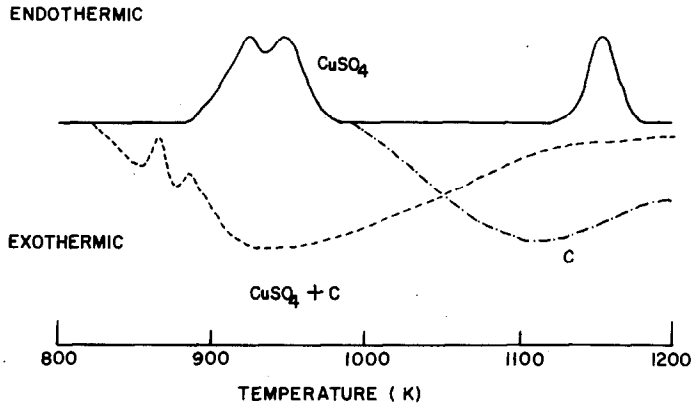

Fig. 1. Thermograms from 800 to 1200 K for copper sulphate (——), copper sulphate/graphite mixture (-----), and graphite (—·—).

gible level, the change in free energy ΔG was sufficient for the reduction of all metal oxides over a wide temperature range. However, the presence of finite partial pressures of carbon monoxide in the system, and other kinetic factors, could limit the extent of reduction. To minimize these effects, a metal oxide was chosen for the reduction of which the standard free energy change ΔG° was negative in the temperature range accessible with the DTA apparatus, thereby ensuring a favourable driving force for the reaction even in the presence of trace amounts of carbon monoxide. Finally, the appearance temperature of the metal must be higher than the temperature range for these reactions to avoid complications due to the vaporization of the analyte. Copper sulphate ($CuSO_4$) was selected because it meets these requirements, in that significant conversion into copper oxide (CuO) occurs at 900 K,[6] ΔG° is negative for the graphite reduction at temperatures as low as 400 K and the reported appearance temperature for copper (Cu) is 1730 K.[2]

Figure 1 shows the thermograms of copper sulphate ($CuSO_4$), graphite and a 1:3 molar ratio mixture of the two. The thermogram of copper sulphate showed the conversion of the salt into copper oxide through a $CuO \cdot CuSO_4$ intermediate[6] at approximately 900 K, followed by the formation of Cu_2O at 1150 K. In the thermogram of graphite there was only a large exothermic peak beginning at 1000 K, which was the result of oxidation of the graphite by trace amounts of oxygen in the system. While thermodynamics predict that this reaction could occur at lower temperatures, reaction kinetics control the rate of this reaction below 1370 K.[7] The thermogram of the $CuSO_4$/graphite mixture showed a series of exothermic peaks beginning at 825 K. The first two peaks are believed to be due to the decomposition of the sulphate in the presence of graphite to CuO, the mechanism being that cited above for the decomposition of $CuSO_4$. The large peak extending from 870 to 1100 K is attributed to the reduction of CuO by graphite to metallic copper. To confirm this hypothesis, DTA was used to examine a CuO/graphite mixture and these results are presented in Fig. 2. The thermogram of CuO showed that it underwent no reactions until 1150 K was reached, when Cu_2O was formed. When a 1:1 molar ratio mixture of CuO and graphite was examined, a large exothermic peak beginning at 850 K was recorded. The location of this peak was similar to that recorded for the $CuSO_4$/

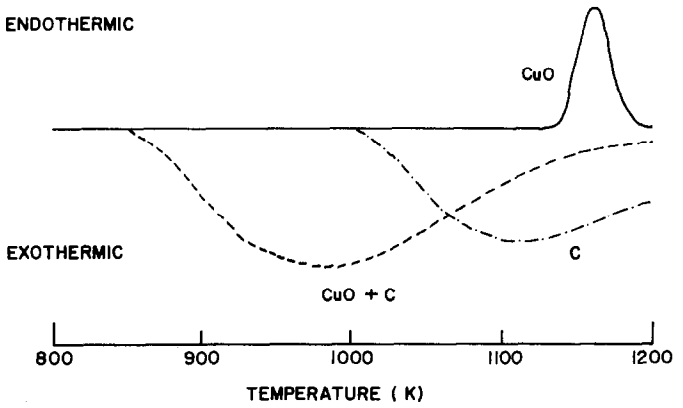

Fig. 2. Thermograms from 800 to 1200 K for copper oxide (——), copper oxide/graphite mixture (-----), and graphite (—·—).

graphite mixture. Reduction of CuO to Cu by the graphite is believed to be responsible for this exothermic peak. When graphite was present in the CuO sample, the peak which corresponded to the formation of Cu_2O was greatly diminished, thus indicating that the amount of CuO in the sample had decreased. If the CuO/graphite mixture was subjected to two consecutive heating cycles, the exothermic peak corresponding to the reduction of CuO was absent during the second cycle. While thermodynamics predict that reduction of CuO by graphite should occur at a temperature as low as 400 K, the fact that it did not occur until 850 K was reached suggests a kinetic control of this reduction process, similar to that discussed earlier for the oxidation of graphite.

Additional evidence for the occurrence of this reduction process was obtained by ESCA experiments to examine the oxidation state of Cu on the atomizer surface. For these studies, a 2.0-μl sample of a 100-ppm Cu solution (the sulphate was used) was pipetted onto the atomizer surface and then desolvated. The binding energy of the Cu peak was then determined by X-ray photoelectron spectroscopy. Repetition of the experiment in which the sample was first desolvated and then heated to 1000 K for 15 sec revealed a 2-eV reduction in the binding energy of the Cu peak located at 934 eV. This shift to lower energy is indicative of a two-electron process, which again could be accounted for by CuO being reduced to Cu metal by the graphite.

CONCLUSIONS

From these studies, it can be seen that graphite reduction of the metal oxide may occur at relatively low temperatures. Therefore, appearance temperatures observed for many metals depend on the vapour pressure and not on the actual reduction process. Instrumental factors such as heating rates and atomizer geometry may cause slight shifts in these appearance temperatures. Theoretical models of the vaporization process assume that the analyte is present on the atomizer surface as the free metal.[8–10] Using the criterion put forward by L'vov[11] that vaporization takes place rapidly when the partial pressure of the metal is equal to or greater than 0.1 mmHg, a fair correlation between predicted and measured appearance temperatures can be made for about half the elements studied by Aggett and Sprott.[1] Deviations from these predictions will occur for metals such as Mg where the oxide sublimes before reduction takes place or for metals such as Al where the strength of the metal oxide bond is so large that vaporization takes place as soon as reduction occurs.

This study of graphite reduction may assist in the evaluation of potential errors in analysis by flameless atomic-absorption. For example, selection of the proper ashing conditions can be very important. Even though the vapour pressure of the metal oxide may be insignificant at the ashing temperature, the metal formed in the reduction process may have a significant vapour pressure under the ashing conditions. This would result in serious errors due to the volatilization of the analyte before the atomization step.

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ANNOTATION

INFLUENCE OF THE SOLVENT ON THE NATURE OF THE EXTRACTING SPECIES

INVESTIGATION OF NICKEL-PHENANTHROLINE/BIPYRIDYL-ROSE BENGAL SYSTEM

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Summary—Nitrobenzene is found to extract nickel in the presence of 1,10-phenanthroline and Rose Bengal as an ion-association complex $[Ni(Phen)_3^{2+}:2RB^-]$ and not as the complex $[Ni(Phen)_2^{2+}:2RB^-]$ reported earlier as extracted into chloroform. The molar absorptivity of the nitrobenzene extract is markedly higher than that of the chloroform extract. The difference in the composition of the extracted species is very interesting. A general scheme is proposed to explain this difference on the basis of the donicity and dielectric constant of the solvent. Beer's law is obeyed in the range 0.05–1.05 ppm of Ni. Interferences of some cations and anions have been studied. Similar observations apply when 2,2′-bipyridyl is used in place of 1,10-phenanthroline.

Ion-association complexes with dye anions are increasingly investigated because of the high molar absorptivity when they are extracted. In general aromatic or chlorinated hydrocarbons are used for extraction, usually nitrobenzene or chloroform.[1]

Nickel is extracted into chloroform in the presence of 1,10-phenanthroline and Rose Bengal, the extracted species having a composition 1:2:2 (Ni:Phen:dye).[2]

It is now observed that when nitrobenzene is used for the extraction, both the composition and the molar absorptivity are changed. The corresponding bipyridyl system behaves similarly.

EXPERIMENTAL

Reagents

Nickel, 1,10-phenanthroline and 2,2′-bipyridyl solutions (0.01*M*) were prepared from analytical-grade reagents in doubly distilled water, slightly acidified with sulphuric acid. A $1 \times 10^{-3}M$ solution of Rose Bengal extra was prepared by dissolving the required amount in doubly distilled water rendered slightly alkaline.

All the solvents were distilled before use.

Procedure for determination of nickel

To a known volume of nickel solution (containing 1–11 μg of nickel) in a 120-ml separatory funnel, add 2.0 ml each of $1.0 \times 10^{-3}M$ Rose Bengal and $1.0 \times 10^{-3}M$ 1,10-phenanthroline or 2,2′-bipyridyl and 2.0 ml of 1*M* sodium sulphate. Adjust the pH to 7.0 and dilute to 20 ml with distilled water. Shake the solution with 20.0 ml of nitrobenzene for 2 min. After separation, centrifuge the organic phase and measure its absorbance at 570 nm, against a similarly prepared reagent blank.

RESULTS AND DISCUSSION

It is observed that nickel is not extracted into any solvent in the presence of either 1,10-phenanthroline (or 2,2′-bipyridyl) or Rose Bengal only. Chloroform and nitrobenzene extract nickel in the presence of both 1,10-phenanthroline (or 2,2′-bipyridyl) and Rose Bengal, giving a pink extract, but n-hexane, benzene and carbon tetrachloride do not. Shaking for 1 min is sufficient for quantitative extraction. Alcohols, ketones and esters extract the dye itself. The formation of a third phase at the interface is observed in the case of diethyl ether and *o*-dichlorobenzene, but no extraction.

Absorption spectra

Figure 1 shows the absorption spectra of the nickel–phenanthroline–Rose Bengal and nickel–bipyridyl–Rose Bengal complexes in nitrobenzene and chloroform, recorded against the respective reagent blanks. The wavelength of maximum absorption for both systems is 570 nm. The molar absorptivities of the phenanthroline and bipyridyl complexes in nitrobenzene are 1.0×10^5 and 1.1×10^5 $l.mole^{-1}.cm^{-1}$ (both at 570 nm) respectively. The molar absorptivity of the phenanthroline complex in chloroform was reported to be 5.0×10^4 $l.mole^{-1}.cm^{-1}$ (at 570 nm).[2,3] Beer's law is obeyed (for nitrobenzene solutions) over the ranges 0.05–1.05 and 0.05–0.9 μg/ml for the phenanthroline and bipyridyl systems respectively.

Optimum pH for extraction

The optimum pH for the extraction of the complexes into nitrobenzene is 6.5–7.5. Easy separation of the two phases and hence reproducible values for absorbance are facilitated by making the aqueous phase 0.1*M* in sodium sulphate.

Concentration of the reagents

A fivefold molar excess of the reagents is sufficient for quantitative extraction of nickel into nitrobenzene.

Composition of the species extracted

The ratios of the components in the complex extracted into nitrobenzene were determined by Job's method of continuous variations and were found to be 1:3:2 (Ni:phenanthroline:Rose Bengal). Similar results were obtained for the bipyridyl complex. When chloroform is used as the solvent, a slight amount of solid is observed at the interface. Because of this, reproducible results were not obtained. However, when the aqueous phase was analysed, the Job curves indicated a composition of 1:2:2 (Ni:Phen:RB) in agreement with the earlier reports.[2]

According to Gutmann, chloroform has donicity number zero and acceptor number 23.1, while those for nitrobenzene are 4.4 and 14.8 respectively.[4] Because of the high dielectric constant of nitrobenzene, the distance between the cationic and anionic components of ion-association complexes in nitrobenzene medium is large compared to that in chloroform, the dielectric constant of which is low. In view of the donor properties of nitrobenzene, it is assumed that the solvent co-ordinates with the metal in 2:1 ratio and is subsequently displaced by phenanthroline:

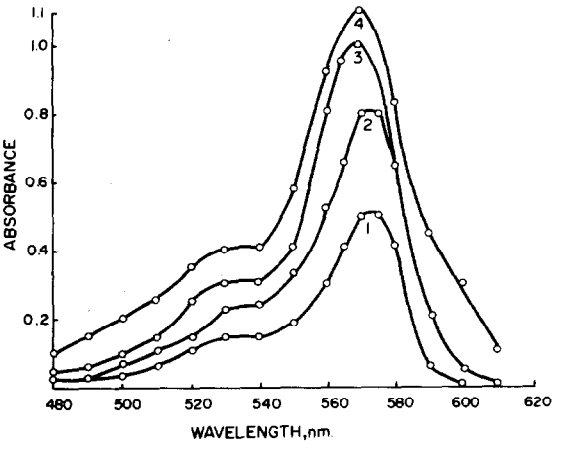

Fig. 1. Absorption spectra of the nickel complexes in chloroform and nitrobenzene at pH 7.0: Nickel $1.0 \times 10^{-5}M$, phenanthroline or bipyridyl $5 \times 10^{-5}M$, Rose Bengal $5 \times 10^{-5}M$. 1. Nickel–phenanthroline–Rose Bengal complex in chloroform. 2. Nickel–bipyridyl–Rose Bengal complex in chloroform. 3. Nickel–phenanthroline–Rose Bengal complex in nitrobenzene. 4. Nickel–dipyridyl–Rose Bengal complex in nitrobenzene.

$$(A)\quad Ni(Phen)_2^{2+}.2A^- \xrightarrow[\text{chloroform}]{\text{in}} [Ni(Phen)_2^{2+}]_s.[2A^-]_s$$

s = solvent molecules; A = the dye anion

$$(B)\quad Ni(Phen)_2^{2+}.2A^- \xrightarrow[\text{nitrobenzene}]{\text{in}} [Ni(Phen)_2(NB)_2^{2+}]_s.[2A^-]_s$$

NB = nitrobenzene

$$[Ni(Phen)_2(NB)_2^{2+}]_s.[2A^-]_s + Phen \rightarrow [Ni(Phen)_3^{2+}]_s.[2A^-]_s.$$

Evidence of this type of solvent displacement can be found in the work of Harris and McKenzie.[5] Further, Natarajan *et al.*[6] observed that octahedral $RuCl_2(AsPh_3)_2L_2$ ($L = N_2H_4$, $C_6H_5NHNH_2$, NH_3 or CH_3NH_2) complexes decomposed in solvents such as chloroform and dichloromethane, and Masoud[7] reports that octahedral nickel complexes are not affected when dissolved in nitrobenzene.

Interferences

Acetate, citrate, chloride, nitrate, phosphate and tartrate do not interfere even when present in 500-fold ratio to nickel, but perchlorate, even at low concentrations, interferes seriously because $Ni(Phen)_3^{2+}$ forms a colourless ion-association complex with it in preference to the dye. Al^{3+}, Ba^{2+}, Mg^{2+} and Cr^{3+} do not interfere, even when present in 100-fold ratio to nickel, but Co^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} interfere seriously.

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PRELIMINARY COMMUNICATION

A NEW TITRANT FOR PERCHLORATE: CETYLTRIMETHYLAMMONIUM BROMIDE *

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Summary - Cetyltrimethylammonium bromide is used in the precipitation titration of perchlorate, with potentiometric end-point detection. A perchlorate, fluoroborate or nitrate ion-selective electrode may be used. The method is more sensitive than the commonly used titration with tetraphenylarsonium chloride. It can be used over the pH range from 1.20 to at least 12.8. The titrant is much cheaper than tetraphenylarsonium chloride.

Baczuk and Dubois in 1968 reported the potentiometric titration of 1.5 - 2 mmole of perchlorate with 0.05M tetraphenylarsonium chloride.[1] The indicating perchlorate ion-selective electrode (ISE) was an Orion model 92-81; the reference electrode was a double-junction model in which the salt bridge was filled with ammonium nitrate solution.

Smith and Manahan[2] used the same electrode system and titrant strength. They considered the limit of this method to be near 0.25 mmole of perchlorate per 50 ml of solution. They were, however, able to lower this limit to 0.05 mmole per 50 ml by operating at 2°. This decreased the solubility of the tetraphenylarsonium perchlorate and thus enhanced the steepness of the titration curve.

We have already evaluated tetraphenylarsonium chloride, tetraphenylphosphonium chloride and tetra-n-pentylammonium bromide for the potentiometric determination of perchlorate.[3] We found the two tetraphenyl salts equivalent, yielding the same precision and magnitude of potentiometric breaks; considerably smaller breaks were obtained with tetra-n-pentylammonium bromide. In that work we lowered the limits for the potentiometric titration of perchlorate with the tetraphenyl salts to approximately 0.09 mmole per 50 ml. If Gran plots are used, this limit can be further lowered to near 0.01 mmole per 50 ml.

Recently we have reported use of 1,2,4,6-tetraphenylpyridinium acetate (TPPA) as a new titrant for some large anions, including perchlorate.[4] Although this compound can be fairly easily synthesized,[5] it is, to our knowledge, commercially available from only a single source.

Schaak and Wagner[6] reported a gravimetric method for fluoroborate, based on cetyltrimethylammonium chloride as precipitant. The solubility of the precipitate was only a tenth of that of the corresponding nitron salt. However, the precipitate could not be dried to

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constant weight so excess of precipitant was added, and after the filtration, this excess was, in turn, precipitated with an excess of ferrocyanide. After filtration, the excess of ferrocyanide was titrated with permanganate. The interfering anions were those also precipitated by nitron: molybdate, tungstate, perchlorate, etc. It seemed to us surprising that large quaternary amine salts had not been tested for use in the precipitation titration of large anions such as perchlorate, with ISEs for end-point detection. Quaternary amine salts such as cetyltrimethylammonium bromide (CETAB) are commonly available and considerably cheaper than the fairly expensive tetraphenylarsonium chloride (ϕ_4AsCl). Thus, 2000 ml of the 0.05M titrant will cost $1.32, compared with $96.30 for the equivalent amount of ϕ_4AsCl solution.

The 92-series ISE has recently been replaced by a 93-series model, which is less sensitive to air-bubbles and static electricity, does not require periodic refilling with two filling solutions, and has a longer operating life. Therefore, in the following work the 93 model was used.

EXPERIMENTAL

Reagents

The titrants were approximately 0.05M aqueous solutions of tetraphenylarsonium chloride (ϕ_4AsCl), tetraphenylpyridinium acetate (TPPA), and cetyltrimethylammonium bromide (CETAB), standardized against ammonium perchlorate. CETAB can also be standardized by potentiometric titration with silver nitrate.

Apparatus

The titration system was controlled by a Tektronix 4051 graphics system as previously described.[4] The emf was monitored with an Orion model 93-81 perchlorate ion-selective electrode (ISE) and a double-junction reference electrode (salt bridge 0.1M ammonium fluoride). The Orion model 93-05 fluoroborate and 93-07 nitrate ISEs are also suitable.

The magnetic stirrer motor was separated from the titration vessel by a water-cooled plate and an earthed aluminium plate.

Procedure

Samples were pipetted into a 50-ml beaker containing a stirring bar and diluted to 25 ml with distilled water before titration at room temperature (23 ± 1°). Titration end-points were calculated according to Savitsky and Golay.[7] The convolute used was for a third-order second derivative and 25 points. The zero crossing was found by linear interpolation in the region near the change of sign.

RESULTS AND DISCUSSION

Representative titration curves for 0.05 mmole of ammonium perchlorate (AP) with CETAB, ϕ_4AsCl, and TPPA are shown in Fig. 1. Although the magnitude of the potentiometric breaks is quite similar, the CETAB solution yields a slightly steeper titration curve. This is confirmed by Table 1 which presents statistics for the standardization of the three titrants. With 0.05 mmole of AP the lowest standard deviation was obtained with CETAB, followed by ϕ_4AsCl, and finally TPPA. For larger amounts of AP (approximately 0.20 mmole), the standard deviations for the three titrants were similar. It seems, therefore, that the new titrant might prove particularly valuable for low-level titrations.

We have previously found that ISEs containing exchangers based on disubstituted bathophenanthrolines containing 2 benzene rings respond to perchlorate ion, etc.[4] Therefore, the Orion 93-81 perchlorate ISE, 93-05 fluoroborate ISE, and 93-07 nitrate ISE were compared, as shown in Table 2. Because the fluoroborate ISE yielded the lowest standard deviation, it was used throughout this work. A word of caution, however, is in

order: although a sensing module should, according to the manufacturer, last 6 months in normal use, in time the electrode slope will decrease and readings will start to drift. The electrodes we used had been in sporadic use for other work for at least 2 years, and still yielded good responses. A comparison of electrodes under these conditions is difficult, and we cannot state at this point that any of the electrodes is preferable.

Table 1. Titration of ammonium perchlorate by use of the fluoroborate ISE; comparison of titrants

ClO_4^-, mmole	Titrant	Mean molarity	Standard deviation*
0.05	CETAB	0.04809	0.00009
	ϕ_4AsCl	0.04921	0.00025
	TPPA	0.04827	0.00212
0.20	CETAB	0.04871	0.00011
	ϕ_4AsCl	0.05008	0.00005
	TPPA	0.04848	0.00011

* Range method; 3 replicates for 0.05 mmole, 4 for 0.20 mmole.

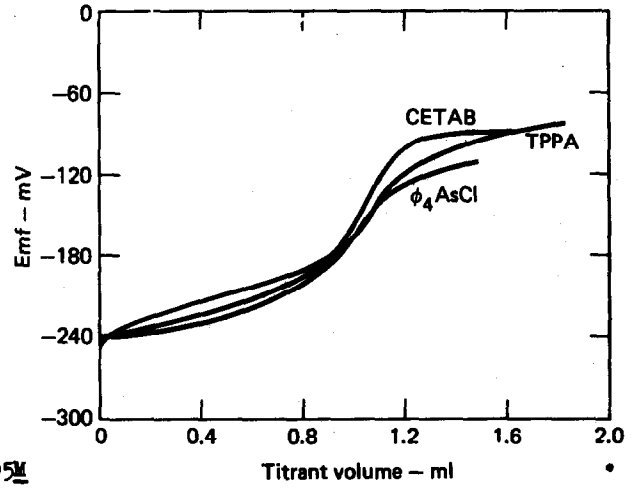

Fig. 1. Titration curves for 0.05 mmole of ammonium perchlorate titrated with the three titrants; fluoroborate ISE.

Table 2. Titration of 0.25 mmole of ammonium perchlorate with 0.05M CETAB: comparison of sensing elements

Sensing element	Mean molarity	Standard deviation	
fluoroborate	0.04877	0.00006	(4)*
perchlorate	0.04885	0.00027	(4)
nitrate	0.04851	0.00011	(5)

* Number of replicates.

We make it a practice to initiate each series of titrations with several known perchlorate solutions. We have found that the first run of a series does not yield emf values as stable and end-point breaks as large as those in subsequent runs. We therefore recommend a study of how the electrode should be stabilized and conditioned to render even the first run reliable.

Table 3. Statistics of the titration of small amounts of perchlorate with 0.05M CETAB, using the fluoroborate ISE

Ammonium perchlorate, mg		$[ClO_4^-]$, M	Mean recovery, %	Standard deviation, %
taken	found			
2.944	2.950	1.0×10^{-3}	100.2 (5)*	0.3
1.178	1.220	4.0×10^{-4}	103.6 (5)	1.1
0.471	0.479	1.6×10^{-4}	101.7 (3)	3.0

* Number of replicates

In Table 3 we present statistics for the determination of small amounts of perchlorate (as AP) by titration with 0.05M CETAB, using the fluoroborate ISE. Even at a perchlorate level of 1.6×10^{-4}M reasonable recoveries are still obtained. This is about an order of magnitude less than the lowest level previously reported.

Most of our titrations were carried out near pH 5.0. Good titration curves were obtained over the pH range from 1.2 to 12.8. At a pH of 0.8 the titration curve was slightly distorted. However, if the titrant is standardized at this pH then good results can be obtained. We previously reported that TPPA can be used over the pH range from 2.2 to 11.0; Baczuk and DuBois[1] recommend a pH range of 4 - 7 for the titration of perchlorate with ϕ_4AsCl.

Further work is in progress with 0.01M CETAB as titrant, and on its applications for potentiometric titration in conjunction with the fluoroborate (or perchlorate or nitrate) ISE. Preliminary experiments have shown that fluoroborate, as expected, can be similarly determined. Although the CETAB fluoroborate is more soluble than the corresponding perchlorate, it is less soluble than tetraphenylarsonium fluoroborate. Organic anions such as nitroform, $C(NO_2)_3^-$, and picrate, and detergent anions such as sodium dodecyl sulphate can also be determined by potentiometric titration with CETAB.

An additional advantage in using CETAB is its lower toxicity (compared to the arsenic compound) and the fact that the perchlorate precipitate does not adhere as strongly as tetraphenylarsonium perchlorate to the electrodes and burette tip. The stability of CETAB solutions over extended periods of time has not yet been investigated.

A limitation, however, is that the electrodes can be used only in aqueous solution.

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TALANTA REVIEW*

THE APPLICATION OF GAS CHROMATOGRAPHY TO FOOD ANALYSIS

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Summary—Gas chromatography is widely used in food analysis, especially for trace analysis, determination of volatiles, and identification of sources of adulteration and undesired flavours. The literature on the applications is reviewed.

Gas chromatography (GC) has been applied to food analysis for almost 30 years. Part of the book "Gas Chromatography In Food Analysis" by G. J. Dickes and P. V. Nicholas (Butterworths, London, 1976) reviewed the applications up to 1974 and this review updates the book and appraises the current situation.

There are many areas of food analysis where it is desirable to detect or determine a number of compounds in a given organic class, and the various chromatographic techniques have invariably constituted the main weaponry in the analyst's armoury. Despite the advent and impact of high-performance liquid chromatography (HPLC) in recent years, GC continues to provide a steady flow of analytical methods. The emphasis in research and application of GC to food analysis has changed according to the problems current at the time. In the 1950s, when the basic technique was still being developed, applications were restricted to the classes of organic compounds used in that development, *e.g.*, amino-acids, fatty acids, hydrocarbons and alcohols. When new detector systems were developed in the late 1950s and early 1960s, with increased specificity and sensitivity designed chiefly to help the pesticide-residue analyst, fashion turned to the detection and determination of food additives and contaminants.

A re-examination of the determination of quality-control parameters came with the development of newer volatile derivatives for GC, *e.g.*, trimethylsilyl derivatives of sugars, and with the formation of derivatives having much lower detection limits than the parent compound, *e.g.*, the *N*-trifluoroacetyl derivatives of amino-acids.

The art has naturally advanced considerably since the early 1950s. Quality control analysis is routine and so is the determination of established additives and contaminants. However, as new additives are formulated and legalized or banned, and as the presence of new contaminants is discovered, GC is an automatically considered method of analysis. Currently, there is renewed interest in the determination of mycotoxins, drug residues and compounds leachable from food-packaging materials.

This review is divided into four parts; the first deals with the influence of food analysis on GC technique; the second covers the determination of those compounds naturally present in foods and used to give an assessment of quality; the third deals with the determination of food additives and contaminants; the fourth is a short conclusion which includes value judgements.

INFLUENCE OF FOOD ANALYSIS ON GC TECHNIQUE

The greatest impact that food analysis has had on improving GC technique has been in detector technology and derivative exploitation. Pesticide-residue analysis was the impetus for the development of such detectors as electron capture (EC), alkali metal flame ionization (AFID), flame-photometric (FPD), and microcoulometric (MCD). The many methylation and trimethylsilylation (TMS) derivative methods have been formulated or improved as a result of demands by the food analyst, as have sampling techniques, such as headspace and preconcentration procedures, *e.g.*, solid trapping. The difficult task of trapping and detecting food volatiles has led to the development of cryogenic temperature-programming and some refinements in capillary column technology.

Injection and sample concentration

Because of the complex matrix of many foods, it is only drinks *e.g.*, alcoholic beverages, that can normally be directly injected into the chromatograph. Not surprisingly, this type of sample is suitable for automatic injection, and Stockwell and Sawyer[1] introduced such a system, with an internal standard added before the injection. This system was a modification of

* For reprints of this review, see Publisher's announcement near the end of this issue.

the one designed by Boer.[2] The system was applied to automatic sampling of tinctures and essences for determination of dutiable spirit.[3]

The direct GC analysis of headspace vapours over food products eliminates the risk of artefact formation in concentration procedures, and is the easiest and most convenient way to study volatile flavour and aroma components. The container can be fitted with a rubber stopper or septum which is penetrated with a syringe needle for sampling.[4–6]

Gases may be sampled with gas-sampling loops or large-volume gas-tight syringes, and specially toughened syringe needles are available for direct insertion into the headspace of food cans and other containers, without opening them. Such a procedure was used by Novák *et al.*[7] for taking representative liquid or gaseous samples from moderately pressurized containers, *e.g.*, canned beverages. The headspace technique was used by Sinclair *et al.*[8] for the determination of dimethyl sulphide in beer. The sample was chilled to 0° and mixed with sodium chloride, and n-butanol was added as internal standard. The mixture was left at 30° for 1.5 hr before the headspace was sampled.

Fore *et al.*[9] and Dupuy *et al.*[10] used the headspace technique for the determination of residual propan-2-ol and acetone in oilseed meals and flours. Headspace above wine was analysed for volatiles by Bertuccioli and Montedoro,[11] who used a 2-litre syringe as container and so could sample the vapour directly; the sample was passed through a Porapak Q trap to remove ethanol and water, which would otherwise swamp the other volatiles.

For the detection of trace components some advantage may be obtained by using the cryogenic injection technique of Rushneck[12] in combination with large headspace samples.[13] In this procedure, successive injections are made into the GC and the sample is condensed at low temperatures in the initial portion of the column. After temperature-programmed GC the trace components are thus accumulated in amounts sufficient for detection.

A novel technique was used by Senanayake *et al.*[14] for analysis of the root, stem, bark and leaves of *cinnamon zeylanicum* for terpenes. Between 15 and 60 mg of thin strips of plant material were placed in a stainless-steel gauze basket fitted inside the injection port, and the unit was heated at 180° for 5 min, with the GC column kept cool; the volatiles were then swept on to the column. β-Caryophyllene was detected in greater amount by this technique than by others which required sample treatment.

Brown *et al.*[15] also used a liner as a pre-column for the study of volatiles from peanuts. Such pre-columns in the form of packed injection-port liners have been used extensively in the GC determination of volatiles where it was necessary to remove the non-volatile material. A large sample was diffused into a packed liner, which was inserted in the heated injection port so that the volatiles could be swept directly on to the column. Injection-port liners packed with sand were used initially but glass wool appears to be favoured.[16] Dupuy *et al.*[17] trapped the volatile components of salad oils and shortenings in a glass liner containing glass wool. The liner was subsequently placed in the inlet system of the GC and the volatiles released at 120°. Besides the natural components there would be any residues of solvents, *e.g.*, aliphatic hydrocarbons. Hexane residues, when present in vegetable oils, can be released by this method.[18] Bonney *et al.*[19] used a system of concentric liners, *i.e.* an inner one of glass surrounded by one of stainless steel, when examining hop extracts for methyl esters of fatty acids. Non-volatile material trapped in the liners could be periodically removed.

The limitation of headspace analysis can be the requirement of exceedingly large volumes of headspace vapour for detection of trace amounts of many components. The minor components may be so diluted with carrier gas that they escape detection. Low-temperature GC pre-columns are often used to concentrate headspace vapours.[20,21] Such a method for concentration was chosen by Morgan and Day[22] in the analysis of flavour volatiles. A screw-capped vial containing sufficient anhydrous sodium sulphate to saturate the aqueous sample was left overnight in an oven at 105°. The sample was then added, a drilled cap containing a silicone rubber liner was fitted and the vial was attached to the apparatus. The vial was heated to the desired entrainment temperature and agitated intermittently. Carrier gas was passed through the apparatus into the GC column where the volatiles were condensed in the initial portion of the column, which had been cooled in solid carbon dioxide. At the end of the entrainment period the column was disconnected from the apparatus and coupled to the GC injection port. The oven was heated to the analysis temperature and GC carried out in the usual manner.

The other important technique for concentration of volatiles is adsorption on an activated solid, such as charcoal.[23,24] Hartman *et al.*[25] isolated and concentrated volatiles from vegetable oil by bubbling helium through the sample, heated to 350°. The volatile components were collected in activated charcoal over a period of 2 hr and then extracted with carbon disulphide containing an internal standard. A 400-fold concentration of the volatiles was achieved with this procedure, which gave good reproducibility.

The development of porous polymers as trapping materials in GC (because of their adsorption and retention properties) has led to a greater use of the solid trapping technique. Murray[26] concentrated headspace volatiles from wines and spirits on various adsorbents, including Chromosorb 102, 105 and 106 and also Tenax GC (2,6-diphenyl-*p*-phenylene oxide). Novotny *et al.*[27] used Tenax GC to concentrate the volatiles of dried sage leaves.

Alumina and acid-washed Celite 545 were both used as adsorbents by Clark and Cronin[28] for trapping flavour volatiles. The open-tubular glass column

containing the adsorbent was disintegrated in a small volume of water to release the volatiles for GC analysis. A combination of solid and liquid trapping was used by Jennings *et al.*[29] to isolate beer volatiles. The headspace sample was trapped on a small Porapak column which was subsequently back-flushed at 100° with carrier gas, the volatiles being condensed in a cold trap. This double preconcentration was necessary to remove ethanol, which otherwise interfered with the separation of the minor components.

Controlled rate of injection through a pressure-lock system was used by Grob and Grob[29] to prevent decomposition of mustard oil from radishes.

Column materials and temperature programming

Food analysis had little impact on the early development of columns, which was mainly done by the petroleum industry. The analysis of polar compounds, however, which is the main concern of the food analyst, has required some further exploration.

In a study of column efficiency for determination of polychlorinated biphenyls (PCBs) and fatty acid methyl esters, Onuska and Comba[30] modified open tubular glass columns by etching the internal surface with hydrofluoric acid to increase the surface area. The resulting "whiskered" column walls produced an excellent surface for coating. Similar columns were used by Schieke and Pretorius[31] for separation of essential oil components.

It is well known that certain metal columns can cause breakdown of some compounds during GC. Glass columns are generally accepted as non-reactive and Ackman and Sipos[32] have gone a stage further than most workers and incorporated glass linings in the metal connectors in their chromatographs. This refinement aided the separation of the methyl esters of heptadecanoic, heptadecenoic and eicosanoic acids in a lard–corn oil mixture.

Benzotriazole (1% in acetone) has been used to deactivate the stainless-steel transfer lines between column and detector,[32a] to prevent decomposition of thiols present in mixtures of food volatiles.

In a study to obtain an open tubular column coating of maximum separating capacity for the determination of the fatty acid composition of various fatty vegetable oil glycerides, Flanzy *et al.*[33] used Carbowax 20M modified by terephthalic acid to give a layer thickness of 0.1 μm. This gave an efficiency of greater than 70,000 theoretical plates. In the separation of beer volatiles Witheycombe and Lindsay[34] used a 0.03-in. bore open tubular column to increase the capacity of the column coating, compared to the conventional 0.01-in. column. The wider column can carry a loading of 1 mg per peak compared to 5 μg per peak with the narrower one.

The current interest in the erucic acid content of fats and oils has prompted better separation of its methyl ester from the others and Ackman and Eaton[33a] used open tubular columns coated with Silar-5CP to achieve this.

Poly(methyl methacrylate) and a series of polyesters prepared from butanediol and dibasic acids and from alkanediol adipates have been used by Vernon[33b] to separate methyl esters of fatty acids of vegetable oils. These polymers showed a wide range of polarity and high temperature stability, although some, *e.g.*, poly(methyl methacrylate), were inefficient.

In a study of separation of the methyl esters of the fatty acids of rapeseed oil glycerides on a wall-coated open tubular column, Mayzaud and Ackman[35] found that the response with helium or hydrogen as carrier gas was twice that with either nitrogen or argon.

Many ways have been used to overcome adsorption of compounds on the support during GC. Cochrane,[36] in the separation of free fatty acids, incorporated formic acid in the helium carrier gas. It was assumed that formic acid was preferentially adsorbed on the support; there was also the advantage that if any excess was eluted from the column it would not be detected by the FID.

The thermostable cyanopropylphenylsilicone stationary phase, SP-2300, has been used to separate methyl esters of the fatty acids of rapeseed and peanut oils.[35a] The advantage of this stationary phase lies in the relatively short retention times of those compounds containing more than 20 carbon atoms and this results in a speedier analysis.

In an appraisal of polyhydric alcohols as stationary phases for separation of beer volatiles, Verachtert *et al.*[37] found that 10% erythritol was the best of the seven phases tested, overcoming the swamping effect of ethanol and giving good separation of the flavour volatiles.

The separation of 18 alkylamines on various stationary phases modified by trisodium phosphate was studied by Golovnya and Zhuravleva.[38] They used equations relating the retention indices to number of carbon atoms and to boiling points, for evaluation of food aroma components.

The advantages of temperature programming (TP) in GC are well known. The main influence of food analysis in this connection is in cryogenic TP. It is often necessary to use low temperatures in the separation of flavour constituents, and if it is necessary to include the less volatile constituents in the analysis then TP is used, starting at temperatures as low as −80°.[39] The range of cryogenic temperature-programmed GC was widened by Merritt *et al.*[40] to include temperatures starting at −196°, liquid nitrogen being used to cool the column chamber. These workers showed the necessity for employing very low starting temperatures for complete resolution of mixtures containing many volatile components, *e.g.*, those from irradiated samples of beef. Iverson and Sheppard[41] have shown the advantages of normal TP in their separation of the butyl esters of butter fatty acids and also of the methyl esters of the fatty acids of coconut oil glycerides.

An alternative to TP is pressure programming; this has the advantages of instant re-set following a parti-

cular analysis and of less chance of column bleed. Scott[42] used pressure programming to advantage in the analysis of lemongrass oil. Both types of programming can be used together in the analysis of complex essences to obtain increased resolution in a shorter time.[43]

Detectors

The biggest influence of food analysis on detector development is in determination of pesticide residues. The EC detector was initially developed to detect and determine organochlorine (OC) pesticide residues and the previously low sensitivity in organophosphorus (PO) pesticide residue analysis gave the impetus for the development of the AFID, FPD and MCD.

Alkali metal flame ionization detector. In addition to its normal use in OP pesticide residue analysis, the AFID has been used by Lakota and Aue[44] in the determination of OC pesticide residues. Using a potassium chloride pellet and varying the geometry of the electrodes, Verga and Poy[45] obtained good selectivity between nitrogen and phosphorus in the determination of carbamates, triazines and OP pesticides. Gough and Sugden[46] used a rubidium chloride annulus in order to increase stability of the detector, when examining various foods for nitrosamines. They obtained a sensitivity ten times better than that of the orthodox flame ionization detector, and although the sensitivity diminished with age, it could be restored by cleaning. Kawabata[47] found that using glass connections from the column to the detector improved sensitivity in the determination of nitrosamines in fish products.

Flame photometric detector. The FPD developed by Brody and Chaney[48] has extremely high selectivity for both phosphorus and sulphur, together with adequate sensitivity. This makes it particularly suitable for analyses in which the sample solution contains large amounts of co-extracted material. Thus, the application of this detector to the determination of OP pesticide residues in foods has the advantage that there is no need for extensive clean-up before the GC. As well as for pesticide residue analysis, this detector can be used for the determination of sulphur-containing volatiles. One of the problems with the detector is that the flame is often quenched by the solvent vapour and has to be re-ignited. Hasinski,[49] in determining OP pesticide residues in foods, altered the geometry of the detector so that less than 50 μl of solvent did not quench the flame.

Emission spectrometric detector (microwave plasma detector). This detector was applied to the determination of pesticide residues in foods by Bache and Lisk,[50–53] for both phosphorus and iodine compounds. Because of the high selectivity, full clean-up of food extracts was not always necessary. The same workers applied this detector to the determination of organic mercury compounds in fish.[35]

Electrolytic conductivity detector (Coulson conductivity detector). In the determination of nitrogen-containing pesticide residues, *e.g.*, carbamates, Patchett[55] made several refinements in the basic detector and lowered the limit of detection for nitrogen to 0.1 ng from 1 ng. These refinements were incorporated in the detector used by Cochrane and Wilson[56] for the determination of residues of triazines, substituted ureas and carbamates.

A procedure for the determination of nitrosamines in foods and beverages was suggested by Rhoades and Johnson.[57] The detector was converted for determination of amines by using argon as the carrier gas and substituting an empty quartz tube for the catalyst reactor tube. This unit was operated at 400–600° since in this temperature range ammonia is obtained as a degradation product of many amines and nitrosamines, whereas other organic nitrogen-containing compounds produce virtually none.

In the determination of atrazine residues in potatoes, Lawrence and Moore[58] used a water jacket round the detector, and other refinements, to improve the sensitivity by a factor of five.

The Hall micro-electrolytic conductivity detector has been used in the pyrolytic mode by von Rappard *et al.*[59] for the determination of five nitrosamines.

Microcoulometric detector. Although the main use of this detector was originally in the analysis of organohalogen and organosulphur compounds, it was modified by Burchfield *et al.*[60–62] to determine phosphorus in pesticide residue analysis. In this system, the detector was operated in the reductive mode with molecular hydrogen at 950°, phosphine being formed from OP compounds, and hydrogen sulphide and hydrogen chloride from organosulphur and OC compounds, respectively. All these products could be titrated in the silver-ion cell, and to avoid co-titration when determining phosphorus an alumina column was inserted after the furnace to remove hydrogen sulphide and hydrogen chloride. If silica gel was used in place of alumina, hydrogen chloride was removed and left the phosphine plus hydrogen sulphide to be detected. The MCD is specific and is very useful in residue analysis, particularly where clean-up is difficult.

Electron capture detector. The great interest in OC pesticide residue analysis, which probably reached its peak in the 1960s led to a demand for a detector that was specific and sensitive, and the ECD was devised. Modifications to the detector have been made, OC pesticides or PCBs being used as the analytical models. For example, Brechbuehler *et al.*[63] have produced a micro ECD, reducing the internal volume to approximately 140 μl for use with high-resolution capillary columns.

In a comparison of the efficiency of the ECD with the electrolytic conductivity detector, Lawrence and Ryan[64] used the heptafluorobutanoyl derivative of stilboestrol from beef liver and also carbofuran residues from turnips. They found that the ECD was the more sensitive, but the electrolytic conductivity detector was more selective.

Chemiluminescent detector. Gough *et al.*,[65] in the screening of foods for the presence of volatile nitrosamines, used a chemiluminescent detector which measured the infrared emission resulting from the interaction of NO and ozone. The NO was produced from the nitrosamines by oxidation in a catalytic chamber and then cooled before detection.

The human nose as detector. Much has been written about the sniffing of effluent vapours from GC columns but there has been little attempt to rationalize the technique, which could be put to better use than at present for identification of aroma constituents in foods. Tucknott and Williams[66] have pointed to several disadvantages, which include the distortion of the odour owing to the elevated temperature of the carrier gas, the speed at which one component often follows another, the fact that some components are more concentrated in the effluent than in the original food matrix and also that only one person at a time can conveniently sniff the effluent. To overcome these problems, these workers used 10- or 20-ml disposable syringes for effluent collection, with subsequent dispensing of 1-ml portions to individual aroma panellists.

Derivative formation

Because of the sensitivity and resolving power of GC, the conversion of involatile species into volatile derivatives, though time-consuming, has been found worthwhile. In food analysis, alkylation techniques for fats, and silylation for sugars, are the most important developments.

Alkylation. The formation of alkyl derivatives has probably been the most frequently applied of these procedures, and food has frequently been the medium for experimentation with alkylation techniques. Methylation is most commonly used, followed by propylation and butylation.

Scoggins and Fitzgerald[67] used dimethyl sulphate for the methylation of chlorophenoxyacetic acid herbicides and found it to be quicker and more quantitative than acid-catalysed methylation. A simple procedure for the quantitative methylation of fatty acids from the glycerides in fats and oils was described by Luddy *et al.*[68] It was based on alkali-catalysed reaction of the oil with potassium methoxide in anhydrous methanol. If the free fatty acid content was high, the procedure was modified to include treatment with the acidic catalyst boron trifluoride in methanol after initial reaction with the potassium methoxide catalyst. A similar procedure was used for methylating the fatty acids of the glycerides of peanut oil[69] and of milk fat.[70] Triglycerides of soyabean, safflower and linseed oils were methylated, in a microreactor, by Davison and Dutton.[71] A 3-μl portion of 2.7*M* sodium methoxide in methanol was injected into the microreactor, followed by 2–3 μl of vegetable oil sample. Trans-esterification occurred. This method permits the analysis of microsamples.

Bitner *et al.*[72] methylated fatty acids with tetramethylammonium hydroxide in a microreactor. Churchill *et al.*[72a] used trimethylanilinium hydroxide similarly for methylation of residues of malathion and parathion methyl; the detection limit for these insecticides was 0.4 ng. Sheppard and Iverson[73] have reviewed the various methods of esterification of the fatty acids of glycerides and conclude that careful control of conditions is necessary if artefact formation is to be avoided. They find that artefacts can occur if the temperature of the alkali concentration is too high.

Hydroxyl groups can be converted into methyl ethers by reaction with methyl iodide and silver oxide in dimethylformamide (DMF), a reaction used in the determination of sugars.[74] Fedeli *et al.*[75] prepared the methyl ethers of sterols from the unsaponifiable fraction of olive and sunflower seed oils with dimethyl phosphite in the presence of toluene-4-sulphonic acid.

A chromatographic reaction method for the methylation of OP pesticides was used by Moye.[76] It entailed trans-esterification achieved by injecting the compounds (in methanolic solution) into the chromatograph injection port (at 225°) which contained glass microbeads pretreated with 2*M* sodium hydroxide. Moye[77] had previously used a similar method for the determination of carbamate pesticide residues. In a similar method, Dale *et al.*[78] injected trimethylanilium hydroxide solutions of residues of the insecticide and nematocide, chlorphoxim, obtained from cat-fish, into the chromatograph injection port at 280°. This gave a 70% yield of methyl ester.

Johnson and Wong[79] used a stainless-steel trap containing 10% silver oxide on 60/80 Celite as a reaction chamber for the methylation of the fatty acids of mutton fat. Methyl iodide was injected as methylating agent and the trap was heated at 100° for 2 min to complete the reaction. Diazomethane in a pre-column of alkaline Celite was used by Schwartz and Bright[80] to methylate the fatty acids of milk fat.

Methanolic (3-trifluoromethylphenyl)trimethylammonium hydroxide (0.2*M*) has recently been used as a methylating agent for the trans-esterification of the fatty acids from the glycerides of corn, olive and peanut oils.[80a] The method is rapid and can be carried out at room temperature.

Staruszkiewicz *et al.*[81,82] used boron trifluoride and propanol to form the propyl ester of β-hydroxybutyric acid in the determination of this indicator of putrefaction in eggs. The procedure was a modification of the one used by Salwin and Bond[83] for determination of lactic and succinic acids in eggs. The short-chain fatty acids in butter oil and cheese were determined by Iyer *et al.*[84] by butylation with butanol and sulphuric acid, although it was considered that boron trifluoride would have been a better catalyst.

Halogen-esters. After the realization that the EC detector could be used for other electron-capturing compounds as well as OC pesticides, a conscious effort was made to exploit derivatives containing a large proportion of halogen.

Islam and Darbre[85,86] used the trifluoroacetyl derivatives of the methyl esters of fatty acids in an analysis of protein hydrolysates, these derivatives being formed by reaction with trifluoroacetic anhydride. Trifluoroacetylated mono-, di-, tri- and tetrasaccharides were prepared with *N*-methylhexafluorodiacetamide by Sullivan and Schewe.[87] This reagent, first suggest by Donike,[88] was found to be very satisfactory, and in temperature-programmed GC could separate 13 components from a sugar syrup in 15 min.

Heptafluorobutanoyl esters have been favoured in the determination of steroids at the picogram level. In a study of the sterol contents of virgin and solvent-extracted olive oils, Tateo[89] used the esterification of the sterols with heptafluorobutyric anhydride to produce derivatives of β-sitosterol and stigmasterol, which could be completely resolved and measured by GC. The same reagent was used by Lawrence[90] in the residue analysis of carbamate insecticides, *e.g.*, propoxur and methiocarb.

Silylation. The importance of silylation in GC, *i.e.*, substitution of the active hydrogen in the OH, SH and NH functions by the trimethylsilyl (TMS) group, has increased since its introduction for the preparation of volatile derivatives. The increase in popularity of TMS derivatives is partly due to development of easier methods of preparation. Most of the development work involved pure organic species, and Zuercher and Hadorn[91] compared seven silylation methods, using a mixture of common sugars as the test medium. Sugars may also be reacted with hydroxylammonium chloride to form oximes before silylation. Zuercher *et al.*[92] used this procedure in the separation and estimation of sugars in honey, orange concentrate, grapejuice, and chocolate for diabetics. The silylating agent was heptafluoro-*N*-methyl-*N*-trimethylsilylbutyramide and trimethylchlorosilane.

In a chromatographic reaction method for the separation of cheese volatiles, McGugan and Howsam[93] used a pre-column held at between $-140°$ and $-150°$ and containing 10% OV-101 on 80/100 Chromosorb W-HP. The silylating reagent, *N*-methyl-*N*-trimethylsilylfluoroacetamide was introduced into the pre-column, which was then heated to 180° during 5 min, the ensuing derivatives being swept on to the GC column for separation.

2,4-Dinitrophenylhydrazones. Volatile carbonyl compounds are often important flavour components of foods, accounting for many off-flavours and also pleasant ones. Since the concentration of these volatiles is generally low, they are frequently difficult to detect. Fifteen carbonyls known to be flavour constituents were determined as their 2,4-dinitrophenylhydrazones by Kallio *et al.*[94] It was shown that the ECD gave greater sensitivity and selectivity than the FID.

Oxidation and hydrogenation. Oxidation is not a popular method of derivative formation in GC analysis. However, the oxidation of nitrosamines to nitramines was used to advantage by Althorpe *et al.*[95] They found that nitramines, detected by EC, gave a response about 200 times greater than that for nitrosamines detected by FID. A similar procedure was used by Sen[96] in the determination of dimethylnitrosamine isolated from nitrite-treated fish.

Several different procedures and types of apparatus were described by Beroza and Sarmiento[97] for direct hydrogenation of many organic compounds; some were particularly useful in the quantitative hydrogenation of fatty acid esters of glycerides of vegetable oils. The hydrogenator, which used 1% palladium on 60/80 Gas Chrom P, with hydrogen as carrier gas, was situated in the GC oven and, consequently, operated at the same temperature as the column. Another apparatus used the injection port as reactor so that the temperature could be different from that of the column. Results showed that the hydrogenation procedures were sufficiently powerful to saturate multiple bonds in straight-chain, ring and substituted compounds. If the pre-column was provided with a bypass,[98] so that part of the sample escaped hydrogenation, the original and hydrogenated portions appeared on the same chromatogram. Consequently, the change in retention caused by hydrogenation could be directly observed.

GC IN FOOD QUALITY CONTROL

Most types of food have been analysed by GC. Dairy products, fats and oils, meat, fish, eggs, fruit, vegetables, essential oils, beverages, sugars and cereals are examples of foods for which quality control can be based, in part, on GC. Before the advent of GC, it was not always possible to separate and determine, within a matrix such as food, mixtures of aliphatic acids, amino-acids, sugars, alcohols, esters, ketones, *etc.*, even though these classes of compounds are often present in relatively high concentration. It was also virtually impossible to detect the low concentrations of flavour and other volatile components on which the quality of a large number of foods depends.

Milk, cream and yogurt

Milk is essentially an emulsion of fatty acid glycerides, water, proteins and sugars, and it is logical that milk quality is assessed by the determination of these constituents. The fatty acid constitution of the fatty acid glycerides can be assayed by GC of the free acids or their alkylated derivatives after hydrolysis, or GC of the original glycerides. Although the determination of the fatty acids has been used,[99,100] their relative non-volatility compared with the alkyl esters often causes difficulty and the determination of the methyl or butyl esters is preferred. The three basic methods of methylation are acid-catalysed methanolysis, methanol–boron trifluoride reaction, and methanol–sodium methoxide reaction under sealed conditions. These methods have been critically assessed by de Man,[101] who concluded that losses of lower fatty acids occurred with the first two methods. The third method not only produced satisfactory recoveries of

butyric, caproic, caprylic and capric acids, but also gave better recoveries of linoleic and linolenic acids.

Smith[102] separated the methyl esters of the C_4–C_{18} fatty acids of milk fat, using a small injection volume for one chromatogram but a larger injection for another chromatogram in order to detect the minor constituents, *e.g.*, the C_{13}, C_{15} and C_{17} acids. Glass *et al.*[103] used a trans-esterification technique before GC of the methyl esters of the fatty acids in order to determine the fat content of milk. The technique has particular value when the available sample is small, *e.g.*, <60 mg of milk. The fat is extracted into a mixture of methanol, dimethyl carbonate and benzene, and methyl tridecanoate is added as internal standard. The areas under the peaks are related directly to the area given by the internal standard. Several other workers[70,104–106] have separated the methyl esters of the fatty acids of milk fat. Hadorn and Zuercher[107] use the butyric acid concentration to calculate milk fat content. The milk fat content of milk chocolate was estimated by Iverson.[108] He methylated the fatty acids after saponification and used the lauric acid concentration as a measure of the milk fat content, cocoa butter containing only 0.013% of this acid.

GC of butyl esters of fatty acids was used by Gander *et al.*,[109] and led to exploration of a superior method of preparing butyl esters.[110] The esters were prepared in a few minutes by heating the fat with di-n-butyl carbonate and sodium butoxide and temperature programming was used so that a single chromatogram covered the whole range of fatty acids in milk fat, in contrast to the two chromatograms often required for the separation of all the methyl esters.

Lysine has been determined in heat-treated milk powder after acid hydrolysis of the protein.[110a] The lysine was converted into homoarginine which was chromatographed as the trifluoroacetyl derivative of the butyl ester.

The main interest in the flavour of milk and cream is associated with volatiles which give off-flavours to these products. Patton[111] found δ-deca and δ-dodecalactones in processed milk but not in raw milk, and Arnold *et al.*[112] attributed the stale flavour of stored sterilized milk to lactones, ketones and aldehydes. Mabbitt and McKinnon[113] examined the volatiles produced in milk during storage, using a cold trapping technique and GC, and found that the 2-butanone content increased as souring progressed. An off-flavour of heated milk, termed "cooked", was correlated with hydrogen sulphide production by Thomas *et al.*,[114] using a headspace sampling technique; as little as 10 μg/ml could be detected.

Goitrin, an antithyroid compound, may be found in milk from cattle fed on a diet containing rapeseed meal and can be determined by means of its hexafluorobutyryl derivative and EC detection.[114a]

2-Hydroxy-4-(methylthio)butyric acid residues in milk can be determined after extraction and formation of the trimethylsilyl derivative; FP detection is used (sulphur mode).[114b]

Wong and Patton[115] determined the normal flavour volatiles of cream, and listed methyl sulphide, acetone, 2-butanone and ethanol as important constituents. Hempenius and Liska[116] steam-distilled acetic acid from sour cream before GC determination, and a rapid method for the determination of lactic acid and lactates, as the butyl ester, in whey was used by Gray[117] as an improvement on existing colorimetric methods.

The sugar content of milk has received scant study by GC methods. Lactose was determined by Jaynes and Asan,[118] who used the trimethylsilyl (TMS) derivatives of the α- and β-anomers and the same derivatives were used by Reineccius *et al.*[119] in the separation and determination of glucose, galactose and lactose from whole and skimmed milk. A similar method was used by Mouillet *et al.*[120] in a study of the fate of these sugars, particularly lactose, in the manufacture and storage of yogurt. More recently, the Lane and Eynon method for lactose determination in milk was compared with a GC method utilizing the TMS derivative of the oxime, good agreement being obtained.[120a]

Interest has been shown in the vitamin D content of milk and non-fat dried milk. Janecke and Brendel[121] separated the unsaponifiable matter from the milk and, following clean-up, determined the vitamin as its TMS derivative. Panalaks[122] isolated vitamins D_2 and D_3 from non-fat dried milk and subjected them to GC after modification with antimony trichloride. Vitamin D_2 in full-cream dried milk was determined as its TMS derivative by Bell and Christie[123] after saponification and clean-up. GC has also been used to determine the vitamin C content of infant milk products.[124]

Some concern has been expressed about the possibility of iodine and its compounds finding their way into milk, either through the feeding of cattle with iodine-containing mineral supplements, or by contamination with iodophor disinfectants. In this connection, Grys[125] has produced a GC method suitable for the determination of iodine after its conversion into iodoacetone. A similar method was used by Gabrio *et al.*[126]

Butter

The main interest in butter analysis is whether or not it has been adulterated with vegetable oils or hydrogenated oils and, if so, to what degree. Many analysts have used GC to enumerate and determine the fatty acids present in butter fat and there have been two basic approaches in using the results to discover adulteration.

The first is due to Wolff,[127] who separated the methyl esters of butter-fat fatty acids and introduced the concept of fatty acid ratios as a means of assessing quality. He found that butter contained approximately 3% lauric acid (C_{12}), but palm kernel oil and

coconut oil contained 47–49%. Either this criterion or that of the ratio of lauric to capric acids (C_{12}/C_{10}) was found to give a very good indication of butter purity, the ratio being 1.07–1.13 for 8 French butters compared to 1.64 for butter containing 3% palm kernel oil and 1.96 for butter containing 5% of that oil. Many workers followed Wolff's lead and looked at other fatty acid ratios as indicators of adulteration and it is reported that in genuine butter the ratio $C_4/(C_6 + C_8)$ acids does not exceed 1.8,[128] and that the ratio of unsaturated to saturated C_{18}-acids is close to 3.[129] Methylation techniques improved during the 1960s and the 1968 figures of Luddy *et al.*[68] for pure butter oil were C_{12}/C_{10} acids = 1.18; $C_4/(C_6 + C_8)$ acids = 1.45; C_{14}/C_{12} acids = 4.00 and unsaturated/saturated C_{18}-acids = 2.39.

The second approach was to take the concentration of butyric acid (averaged over many samples) as the standard for 100% butter purity, because margarine and the oils used in its manufacture contain very little butyric acid. In the standard wet chemical method of Reichert *et al.*[130] for assessing butter quality, the fatty acids are divided into three categories, *viz.*, water-soluble volatile, water-insoluble volatile, and water-soluble volatile forming water-soluble silver salts. GC is able to define the acids within each category and leads to a more exact interpretation of quality. Karleskind *et al.*[131] saponified the glycerides and distilled the acidified extract according to the Reichert–Meissl method. The methyl esters were made and GC was applied, with methyl valerate as internal standard. These authors showed that French butter fat contained between 3.2 and 4.0% butyric acid, whereas lard, tallow, palm oil and palm kernel oil contained 0.02, 0.04, 0.01 and 0.03% butyric acid respectively. These results showed that the amount of butyric acid in these oils is equivalent to approximately 1% of that in butter.

Kirschner values, which are directly related to the water-soluble volatile acids which form soluble silver salts, are essentially a measure of butyric acid concentration in butter; Withington,[132] who trans-esterified butter fat with alkaline ethanol, found that the average content of ethyl butyrate from 19 pure butters of various countries of origin was 4.79%. This value was used as the standard for calculation of butter content, particularly where butter was present in other foods at a concentration of 10% or less. Hadorn and Zuercher[133] used a similar method with trans-methylated butter fat.

A semimicro method of determining butter fat in fat mixtures was devised by Phillips and Sanders.[134] They found it simpler to measure free butyric acid after saponification and acidification, obtaining an average figure of 3.6% of the acid for pure butter fat, which is in excellent agreement with Withington's 4.79% for ethyl butyrate. The method was used in the determination of butter fat in such foods as milk chocolate coatings, cream soups, butter confectionery and meat or fish pastes containing butter.

The fact that butter contains no sitosterol, which constitutes the main sterol fraction of vegetable oils, is another means of detecting the presence of margarine in butter. In 1962, Eisner *et al.*[135] extracted sterols from the unsaponifiable matter of margarine–butter mixtures and separated β-, γ- and δ-sitosterol from cholesterol. Using the β-sitosterol peak as a quantitative indicator for margarine, it was possible to detect as little as 0.2% margarine in butter.

Digitonin precipitation followed by acetylation of the sterols was used by Cannon,[136] who separated the acetates of cholesterol and sitosterol and claimed that 2% margarine in butter could be detected. TMS derivatives of the sterols were used by Cerutti *et al.*,[137] who claimed 1% of margarine in butter could be detected. The BSI method for the detection of foreign fats in dairy products[138] is based on sterol analysis; β-sitosterol is used as the indicator, 0.5% being detectable.

The flavour constituents of butter, as found by GC analysis, include δ-lactones,[139–141] aldehydes[142] and indole and skatole.[143] Most work has been carried out on δ-lactone determination and van der Ven[139] concluded that fresh butter contains γ- and δ-keto acids, and that these may be precursors of the corresponding lactones.

Cheese

Most GC investigations of cheese have concerned flavour and aroma and particularly the volatiles responsible for the subtle differences between varieties of cheese. Any interest in fatty-acid analysis of cheese fat is invariably a result of the effect on flavour.

Iyer *et al.*[84] studied the fatty-acid composition of the glycerides of Provolone cheese fat by using GC to separate the butyl esters, and concluded that the short-chain volatile fatty acids were important contributors to flavour. The determination of free acetic, propionic and butyric acids in cheese was subsequently facilitated by using Chromosorb 101 in the gas–solid chromatography (GSC) method of Keen and Walker.[144] Fatty acids can have a deleterious effect on flavour quality and lead to rancidity. It was found by de Man[145] that Cheddar cheese monoglycerides contained short-chain fatty acids and that when the cheese became rancid there was a higher proportion of these monoglycerides present, particularly monobutyrin.

In an examination of cheese for neutral volatile constituents, Liebich *et al.*[146] used the entrainment method, placing the sample in a liner attached to the injector. The liner was held at 190° for 10 min to allow the volatiles to be swept on to the column by the carrier gas, leaving the oil behind. These authors examined the Cheddar, Blue, Roquefort, Romano, Swiss and Limburger varieties and found that methyl ketones were an important flavour group.

As early as 1958, dimethyl sulphide was found in Cheddar cheese[147] and was considered to be an important good flavour factor. GC, coupled with mass

spectrometry (MS), was used by Langler, *et al.*[148] to separate the major volatiles of Swiss cheese. They also found that dimethyl sulphide was an important flavour component, often being present in concentrations above its flavour threshold.

In a series of ripening experiments, Scarpellino and Kosikowski[149] found that the acetic acid and ethanol content increased during the ripening of Cheddar cheese, whereas there was a decrease in the concentration of the trace constituent, acetyl methyl carbinol. Butyric acid, 2-butanol and 2-butanone appeared as ripening proceeded.

Tyramine is an indirectly acting sympathomimetic amine that releases noradrenaline from adrenergic neurones, and it is found in foods such as cheese, red wine and pickled herrings. Kaplan *et al.*[150] determined the tyramine in South African cheeses by GC of its TFA derivative and found that its concentration ranged from 5 ppm for a cream cheese to 775 ppm for a mature Cheddar. Phenethylamine, which is also known as a "migraine precipitant", has been detected in cheese by means of its TFA derivative.[151] Foods containing such sympathomimetic amines must not be consumed by patients taking monoamine oxidase inhibitors as antidepressant drugs.

Animal fats

Lard is probably the most important animal fat, if the interest in its quality is a yardstick. It has been the subject of adulteration by beef and mutton fats, horse fat and many hardened vegetable and fish oils. The GC examination of the fatty acids of lard glycerides has been a popular medium for the testing of preseparation and methylation methods,[68, 152, 153] and also for the assessment of adulteration by tallow or horse fat.[154,155]

Pascussi and Paolini[156] successfully applied the fatty acid ratio to classify pure lard and found that the $C_{14:0+16:0+18.0}/C_{18:2}$ acid ratio lay between 4 and 5, and considered that a value greater than 5.5 indicated adulteration. Similarly, the $C_{18:3}/C_{18:1}$ acid ratio lay between 100 and 200 and values greater than 200 could indicate adulteration. Castledine and Davies[157] used a trans-esterification technique to obtain methyl esters of the fatty acids of a number of animal fats. They calculated the $C_{16:0}/C_{14:0}$, $C_{18:1}/C_{18:0}$, $C_{18:1}/C_{14:0}$ and $C_{18:1}/C_{16:0}$ acid ratios for these fats. The $C_{16:0}/C_{14:0}$ and $C_{18:1}/C_{14:0}$ acid ratios are normally greater than 6 for pure lard, whereas beef and lamb tallow give ratios of less than 4. In addition, lard has a greater total C_{18} unsaturated acid concentration than does beef or mutton tallow.

A different approach to determining adulteration of lard was used by Grieco,[158] who specifically looked for branched-chain and minor-constituent fatty acids, which were found to be present in small concentration in beef tallow but absent in lard. Bastijns,[159] in a similar study, found that the concentration of C_{14} and C_{16} branched-chain acids was 5–10 times as high in beef fat as in lard. He also discovered that the total of C_{15} acids present in lard was less than 0.03%, but 0.2–1.0% in beef fat.

In a comprehensive survey of animal fats, Hubbard and Pocklington[160] substantiated the findings of most other workers. In their survey they also included the fatty acid composition of the fats from chicken, turkey, game birds and rabbit.

There is some interest in the adulteration of goose fat with lard, the fatty acid ratios being successfully employed for detection and sometimes simiquantitative estimation.[161–163]

It is virtually impossible to differentiate beef and lamb fats by chemical methods and the chromatograms of the fatty acid methyl esters are very similar, although it is generally acknowledged that beef fat has the superior organoleptic quality. Hoffmann and Meijboom[164] deduced that the major volatiles of both fats were 4-heptenal and 2,6-nonadienal. It can be assumed that the fine differences between beef and lamb or mutton fats must lie in the minor volatile concentrations.

Horse fat has been used to adulterate beef fat. Suitably chosen fatty acid ratios can give strong indications of such adulteration.[157,165]

Vegetable oils and fats

Vegetable oils are used mainly in margarine manufacture, as cooking oils and as salad dressings. The suspicions surrounding the possible harmful health effects of cholesterol, which is present in animal fats, has indirectly created a greater market for vegetable oils, particularly those for the cooking of food. Oils such as corn, cotton seed, soyabean, peanut and sunflower are used for frying, and palm kernel, coconut, soyabean, sunflower and rape seed are used in margarine manufacture. Margarine is also made from hydrogenated vegetable and fish oils.

Much attention has been paid to the purity and fine quality of various vegetable oils and to the presence of vegetable oils in animal fats. In the latter case, while GC of the fatty acids of the various glycerides can establish the presence of vegetable oils in animal fat, a superior method is to look for phytosterol in a GC sterol analysis because its presence indicates the indisputable presence of vegetable oil.

In contrast to the extensive literature on the analysis of the fatty acid and unsaponifiable fraction, the determination of flavour constituents of vegetable oils has received little attention. General methods have been published for the determination in vegetable oils of lactones at the 1 ppm level[166] and of various carbonyl volatiles by means of their 2,4-dinitrophenylhydrazones.[167]

The neutral volatiles of mayonnaise have been separated after trapping of the acidic volatiles on a pre-column of glass wool coated with sodium bicarbonate.[168] Aliphatic alcohols and aldehydes were predominant among the 21 volatiles identified.

Before hardened vegetable and fish oils were

exploited, margarine was produced largely from mixtures of coconut and palm kernel oils. The lauric acid concentration in the glycerides of both these oils is approximately half that of the total fatty acids. Glyceride and fatty-acid analyses of both coconut and palm kernel oils have been the subject of study by many workers.[169–172]

Some vegetable oil monoglycerides, which result from the enzymatic splitting of some of the triglycerides, are important because they can influence the rheological properties of emulsified oils, *e.g.*, margarine. Halvarson and Ovist,[173] in a GC method for the determination of monoglycerides, found that coconut and palm kernel oils contained the abnormally high level of 0.5% monoglycerides, which made them eminently suitable for margarine manufacture.

There has been recent interest in the GC determination of *trans* unsaturated fatty acids in margarine, primarily to check the existing infrared method. Ottenstein *et al.*[174] used OV-275 as stationary phase to achieve the separation of the methyl esters of *trans* and *cis* isomers of oleic, linoleic and elaidic acids. The same stationary phase and also Silar IOC and SP-2340, two other cyanosilicone phases, which are highly polar and thermally stable, were used by Conacher *et al.*[175,175a] in a similar analysis of margarine. Geometric isomers of unsaturated fatty acids have also been separated after trans-esterification with sodium methoxide.[175b]

Analysis of the unsaponifiable matter of coconut and palm kernel oils has yielded useful information about their triterpene alcohol and sterol content.[176–178] Fedeli *et al.*[178] investigated the unsaponifiable matter of all the common vegetable oils. They found that coconut oil contains β-amyrin, whereas palm kernel oil does not, and this could be used as a distinguishing feature, if required. The volatile flavour constituents of coconut oil have been isolated by Allen,[179] who considered that, among the methyl ketones and lactones identified, δ-octalactone was largely responsible for the typical coconut flavour and aroma.

Whereas palm kernel oil is made from the nut part of the fruit, palm oil is made from the outer flesh. Some study has been made of its glyceride fatty-acid composition,[169,171,172] palmitic acid being the major constituent, and also of its unsaponifiable matter.[176–178]

Cocoa butter and illipe butter contain stearic acid as the major fatty acid constituent of their glycerides. Cocoa butter is used in chocolate manufacture and, on occasion, has been adulterated with coconut and palm kernel oils. The glyceride fatty acid composition of pure cocoa butter has been deduced[180–182] and Iverson[183] showed that the difference in lauric acid content of the cocoa butter and these added oils could be exploited analytically. Coconut and palm kernel oils contain approximately 50% lauric acid whereas cocoa butter contains only approximately 0.01%. Since it is possible by GC to detect 0.25% of lauric acid, it should be possible to detect addition of 0.5% of either of the two oils to cocoa butter. The sterol content of the unsaponifiable matter of cocoa butter has been determined by Fincke[184] and the triterpene alcohols have also been separated.[178]

Those oils which have a predominance of glyceride oleic acid include olive, peanut, almond kernel, peach kernel and hazel nut. Olive oil is the major ingredient of the majority of salad oils and finds particularly good commercial outlets in Mediterranean countries. Because of its commercial importance, it is prone to blending with inferior quality olive oils or adulteration by other cheaper vegetable oils. A large amount of work has been done on evaluating the glyceride fatty-acid composition of olive oil, that of Youngs and Subbaram[180] and Hivon *et al.*[185] being particularly noteworthy.

When it is suspected that low-quality olive oil has been used to supplement the top-grade product, an analysis may reveal the presence of elaidic acid, which is produced by the isomerization of oleic acid, this being encouraged by the heat treatment used to extract low-quality oil; Averill[186] employed GC to separate methyl oleate and methyl elaidate and detect and adulteration. The adulteration of olive oil with seed oils was investigated by Galanos *et al.*[187] Argentation–silica gel thin-layer chromatography (TLC) of the poly-unsaturated glycerides was followed by GC of the methyl esters of the fatty acids containing four or more double bonds. In pure olive oils, this fraction contained 35–37% linoleic acid, whereas the same fraction of most seed oils contained 65–70%.

The sterol and triterpene alcohol analysis of the unsaponifiable matter has been evaluated by Karleskind *et al.*[176] and by Fedeli *et al.*[178]

The importance of the quality of olive oil is illustrated by the 1972 world production of 1.4×10^6 tonnes. For quality assessment, the aroma constituents were determined by Flath *etal.*,[188] who listed 77 components, identified by GC–MS.

Gonzalez-Quijano *et al.*[189] used a headspace technique to trap the volatiles of 13 different varieties of Spanish olive oil for statistical evaluation of organoleptic tests with components identified by GC.

Peanut oil is extensively used as a cooking and frying oil and its glyceride fatty-acid composition has been evaluated.[181] Tests for the presence of peanut oil in other oils, *e.g.*, sesame oil, usually depend on the presence of arachidic and lignoceric acids in peanut oil and their virtual absence in seed oils, the determination of these acids being conveniently carried out by GC. Fedeli *et al.*[178] have determined the triterpene alcohol composition of peanut oil and Murata[190] has analysed the triglycerides.

The free fatty acid content, expressed as oleic acid, was determined by Phillips and Singleton by GC of the methyl esters, with SP-2340 as the stationary phase.[190a]

Peanuts have been used to adulterate sesame seeds, and Letan *et al.*[191] used methylation of the glycerides

and a urea-complexation method before GC in order to concentrate the methyl behenate. Under standard conditions peanut oil was found to contain between 2.3 and 4.3% behenic acid, and sesame oil a maximum of 0.3%. This difference was used to detect the presence of peanuts in tehina and halva, which are sesame-seed products. Sesame oil is used as a frying oil and also as an ingredient of some margarines and its glyceride fatty-acid composition has shown that it contains mainly linoleic and oleic acids, in approximately equal proportions.[171,172]

Cotton seed oil is produced relatively cheaply and is economically important as a margarine ingredient. The glyceride fatty-acid analysis shows that its predominant acid is linoleic.[171,185,192] Schneider *et al.*[193] specifically looked for cyclopropenoid acids and found that 0.5% of the total fatty acid content was malvalic and sterculic acids. Cotton seed oil has been adulterated with such oils as soyabean, rapeseed and rice-bran, and Imai *et al.*[194] used both fatty acid and sterol analyses to detect this adulteration. They found that the presence of erucic acid pointed to rapeseed oil adulteration, and this could be confirmed by identification of brassicosterol. Soyabean and rice-bran oils were detected by means of the presence of linolenic acid and stigmasterol.

Soyabean oil is extensively used in margarine production. Because of this the quality of soyabean oil has received considerable analytical appraisal. The glyceride fatty acids have been determined by several workers,[171,172,185,192,195] and the intact glycerides have been separated by Youngs and Subbaram.[180] In the identification of triterpene alcohols, Fedeli *et al.*[178] found cycloartenol, α- and β-amyrin and cycloaudenol. Soyabean oil is unusual in containing cycloaudenol and not containing 24-methylene cycloartanol and this could be exploited in specifications for the oil. One of the major problems in the storage of soyabean oil is its tendency to autoxidation, which leads to an off-flavour frequently described as "beany". This oxidation is known as reversion and has led to investigation of the compounds which are responsible for the off-flavour. Hoffmann[196] separated the neutral volatiles of the oil into six fractions by GC, and described them in terms of odour. The fraction called "green beans" was further examined by GC and by infrared spectroscopy and was found to contain 3-*cis*-hexenal, which was considered to be the major contributor to the off-flavour. On the other hand, Chang *et al.*[197] attributed the reversion flavour to 2-pentylfuran, which was present in soyabean oil to the extent of 1–10 ppm. Some oil chemists[198,199] have shown that formation of pentane is a good indicator of the presence and extent of decomposition; it presumably arises by autoxidation of methyl linoleate. Even hydrogenated soyabean oil can develop an off-flavour on storage, and Yasuda *et al.*[200] have attributed this mainly to 2-*trans*-6-*trans*-octadienal.

The glyceride and sterol composition of many other oils has been examined by GC, among the more important being corn, sunflower, safflower, linseed, rapeseed and mustard seed oils. The last two are characterized by their high concentration of erucic acid. Separation of the methyl esters of the higher unsaturated fatty acids can be difficult but has been achieved in a rapid automated method for rapeseed oil analysis by Heisz.[201] MS detection of natural erucic acid (as the methyl ester) of rapeseed oil and the ^{14}C-labelled methyl ester added as internal standard has been used to determine erucic acid in the oil.[201a] Rapeseed oil is also characterized by its relatively high concentration of brassicosterol (approximately 8–10% of the unsaponifiable fraction).[176,177]

Fish oils

Fish oils contain relatively high concentrations of unsaturated fatty acids and are hydrogenated before use in margarine manufacture. Many fish oils contain polyenoic acids with up to six double bonds and Lambertsen *et al.*[202] have exploited the different numbers of double bonds of the fatty acids by using TLC before GC. They found that the major acids were $C_{18:4}$, $C_{20:5}$, $C_{22:5}$ and $C_{22:6}$. Many fish oils were also found to contain branched and unbranched C_{17} acids, which are uncommon in vegetable oils. There is such a broad range of fatty acids in fish oils that two chromatograms may be needed to include them all. However, Ackman[203] showed that one chromatogram sufficed with EGSP-Z as stationary phase.

Litchfield *et al.*[204] found that fish oils contain up to 5% of odd carbon-number fatty acids, although mullet is exceptional in containing approximately 10%; vegetable oils contain minimal odd carbon-number fatty acids. Most GC work has centred on herring oil with some attention paid to the oils of capelin, salmon, mullet, tuna, menhaden, pilchard, shrimp and sardine. Gershbein and Singh[205] found that a quarter of the unsaponifiable fraction of herring oil consisted of hydrocarbons, predominantly pristane and squalene. GC has been applied to fish liver oils, mainly for vitamin assay, *e.g.*, the determination of vitamin D in cod liver oil.[206]

Meat

Early studies of meat flavour concerned the considerable contribution from meat fat. Hornstein *et al.*[207] followed the production of free fatty acids in stored cured and cooked meat, using GC of the methyl esters, and related the total acid content to deterioration in quality. Hornstein *et al.*[208] suggested that the volatiles of the lean portions of beef and whale meat were identical, except that the latter contained trimethylamine, and Hornstein and Crowe,[209] in a review on general meat flavour, opined that the volatiles of lean meat of beef, pork and lamb had similar compositions and that the true flavour differences lay in the fatty tissues.

Many procedures have been used for the isolation of meat volatiles before their separation and determination by GC. These include solvent extraction,

cold trapping, trapping in chemical reagents and headspace sampling. El-Gharbawi and Dugan[210] used steam distillation to isolate carbonyls and sulphur-compounds from freeze-dried beef; acetaldehyde, propanal, pentanal, hexanal, acetone, methyl mercaptan and methyl disulphide were positively identified, which indicates the types of volatiles frequently discovered in meat.

Liebich *et al.*[211] used GC coupled with MS to identify roast-beef volatiles in lean and fatty portions. They used vacuum distillation for isolation, followed by solvent extraction, and ultimately identified alkanals, alk-2-enals, alk-2,4-dienals, 3-hydroxy-2-butanone and γ-butyrolactone.

Roedel[211] tried several methods of isolating and concentrating volatiles from raw and roasted beef and concluded that the most efficient was adsorption on glass beads (or Gas Chrom Q) cooled in liquid nitrogen. In the determination, the GC eluate was split so that 90% was sniffed in order to assess the matching of aroma with individual peaks. In the examination of roast beef, he found that the components did not possess the typical aroma and assumed that the flavour and aroma came from a combination of the volatiles.

In comparison with cooked meat, raw meat has little flavour. However, a hot water extract of meat yields a product which has the flavour character of the cooked meat itself and this fact has been exploited commercially in the production of meat extracts. Bender and Ballance[212] used a 2,4-dinitrophenylhydrazine solution to trap carbonyls from a beef extract before application of GC.

Irradiation can be used to preserve meat but there have been problems associated with the production of an off-flavour by this treatment. Wick *et al.*[213] considered that the major contributor to the unpleasant odour and flavour was 3-(methylthio)propionaldehyde. As already mentioned, Merritt *et al.*[40] used a cryogenic temperature-programmed procedure to separate and identify volatiles of irradiated beef.

The components of lamb flavour have not received as much attention as those of beef, but Jacobson and Koehler[214] isolated roast lamb volatiles by cold trapping and GC and used other techniques for identification. The "sweaty" flavour of mutton has been the subject of study by Johnson *et al.*,[215] who considered that 4-methyloctanoic acid was responsible.

The main interest in pork volatiles has been the problem of boar taint. The substance responsible, which has been described as "urine-like" and "sweaty", 5α-androst-16-en-3-one, has been extracted and identified by GC.[216,217]

Volatiles from cured and uncured ham were compared by Cross and Ziegler,[218] who found that carbonyls and sulphur-compounds were predominant in both types. They used either a trapping pre-column of 1% DC-500 on glass microbeads or a series of chemical traps to separate the various classes before GC. In a study of bacon volatiles with a Likens–Nickerson apparatus, Mottram and Puckey[218a] found that the artefacts, 2-methyl-3-nitrobutan-2-ol and its nitrate, were formed from solvent impurities and the oxides of nitrogen produced by nitrite using in the curing process.

The large increase in consumption of chicken has led to interest in its storage and retention of flavour quality, particularly after deep-freezing. Pippen and Nonaka[219] identified n-hexanal and 2,4-decadienal as flavour components worth preserving, and Minor *et al.*,[220] in an examination of the volatiles of cooked breast and leg portions, emphasised the importance of sulphides, disulphides and mercaptans. Nonaka *et al.*[221] obtained cooked-chicken volatiles by isopentane extraction of an aqueous distillate. From 227 peaks, they identified 62 compounds by GC–MS. Hobson-Frohock[222] used a pre-column of molecular sieve 5A to remove aromatic hydrocarbons and branched cyclic compounds before GC of the remaining chicken volatiles. The sieve material was extracted with hexadecane for subsequent analysis of n-alkanes. Chicken carcass has been analysed by GC for n-alkanes in the range C_{12}–C_{33}.[223]

The sulphur- and nitrogen-compounds in meat volatiles were determined with a multi-detector system by Hřivnáč *et al.*[224] The capillary column effluent was split into two streams, and each was split again by metal capillaries; detectors used were FID and FPD, both in different modes, and "sniffing".

In some countries, there is a restriction on the concentration of sorbitol in cooked sausage products, and it has been determined after aqueous extraction and formation of trimethylsilyl derivatives.[224a]

Fish

Other than fish oil analysis, the main application of GC methods to fish is in the study of flavour volatiles. Most fish is transported long distances for sale, and even in iced-storage conditions some bacterial degradation can occur, leading to off-flavours. The commonest volatiles formed as fish ages are amines, particularly dimethylamine and trimethylamine. Examples studied in this context are cod[225–227] and caviar.[288] Mendelsohn *et al.*[20] used different extraction procedures for isolating volatiles from haddock, and found that vacuum distillation gave the greatest yield.

In a study of the carbonyl volatiles of salted salmon and caviar, Golovnya and Uraletz[229] used the system of isothermal retention indices. They used isothermal chromatography at 50° and then at 25° intervals up to 200° and recorded the retention indices at each temperature, the information being used to confirm the identities of the volatiles.

The headspace volatiles of canned tuna have been collected and examined for ethanol content as a means of measuring its spoilage.[230] As spoilage progressed, the size of the ethanol peak increased. Staruszkiewicz found that the spoilage of shrimp can be judged by the formation of indole.[231] He detected

no indole in fresh shrimp and between 0.14 and 1.15 ppm in decomposed samples. The method was later improved by use of a mixture of three internal standards.[231a]

The organoleptic appeal of certain shellfish has been found to be due, in part, to sulphur compounds, *e.g.*, in oysters,[232] and to carbonyl compounds, *e.g.*, in clams.[233]

Fish protein concentrate has become a commercial product and is used in animal feeding stuffs. The degree of "fishiness" is attributed to amines and these have been separated and determined.[234,235]

Eggs

The U.S. Food and Drug Administration has taken particular interest in the quality of eggs in shell. When microbial or enzymic action proceeds in food, aliphatic hydroxy-acids are frequently produced together with other relatively simple organic compounds. Bethea and Wong[236] examined the volatile acid fraction of various quality-graded eggs and detected butyric, isovaleric and valeric acids. By GC of the propyl esters of the aliphatic acids, Salwin and Bond[83] found that fresh eggs contained approximately 4 mg of lactic acid per 100 g of egg and no succinic acid. After the sample had been kept at room temperature for 16 hr the lactic acid content rose to 30.3 mg per 100 g of egg and there was 16.7 mg of succinic acid per 100 g of egg. Further work with this method confirmed these findings.[237, 238] Staruszkiewicz *et al.*[81] found that 3-hydroxybutyric acid could also be used as an indicator of egg decomposition and a collaborative study was conducted to establish that "passable" eggs should not contain more than 0.3 mg of this acid per 100 g of egg.[82]

The benzyl esters of those acids indicative of protein decomposition have been used in GC analysis of eggs.[238a] BCl_3–benzyl alcohol was used in a one-step reaction and has been applied in the determination of formic, acetic, propionic, butyric and isobutyric acids.

The cholesterol content of egg has been used to estimate the egg content of cakes and hamburgers.[239] GC of trimethylsilyl derivatives of sterols present in the unsaponifiable matter showed that whole dried egg had a range of 1.64–1.81% of cholesterol. Provided there was very little or no cholesterol in the other constituents of the confectionery, the dried egg content could be calculated. The egg content of noodles has been estimated by Armandola,[240] on the basis of the fatty acid composition, particularly the oleic/linoleic acid ratio.

Fruits and their products

The analytical interest in fruits is concerned with a variety of organic components which can be divided into macro- and micro-constituents. Classical methods have been used to determine macro-constituents, *e.g.*, sugars and fixed acids. GC methods, although facilitating separation of these constituents, have found their greatest application in the detection and determination of flavour volatiles, which make up the bulk of the micro-constituents.

The major fruit products are extracted oils, which are either purified and added to suitable foods or are diluted with alcohol for use as essences, which are used for the same purpose. GC analysis has had a great impact in the elucidation of the quality of these essential oils, particularly in the detection of terpenes and their oxygenated derivatives.

Fixed fruit acids have been the subject of study by Harvey *et al.*[241] and Fernandez-Flores *et al.*[242] Harvey *et al.* quantitatively separated the methyl esters of malic, citric and oxalic acids extracted from lemon, lime, tomato, grape and prune. Fernandez-Flores *et al.* made ethanolic extracts of fruits, precipitated the acids as their lead salts and converted these into their trimethylsilyl (TMS) derivatives. Concentrations of glycollic, succinic, fumaric, malic, tartaric, citric, syringic and quinic acids in 26 varieties of fruit were determined, and in some instances, the chromatographic "fingerprint" was typical of a fruit or its sub-variety. Among the fruits analysed were apple, pear, grape, peach, plum, prune, cherry, strawberry, blueberry, orange, lemon, grapefruit, melon and banana.

Fernandez-Flores *et al.*[243] have determined of amino-acids in 22 varieties of fruit, including those just listed. They cleaned up the fruit extracts on an ion-exchange resin and used the TFA–n-butyl derivatives for the GC. As little as 0.5 mg of amino-acid per 100 g of fruit could be detected. Kline *et al.*[244] have also analysed these fruits for sugars (*e.g.*, fructose, glucose, sucrose and sorbitol) by GC of the TMS derivatives. The examination of a fruit for fixed acids, amino-acids and sugars by GC yields three sets of data which, taken together, can help in identification of sub-varieties of fruits, and analysis of fruit mixtures.

Fruit pectin was pyrolysed by Zamorani *et al.*[245] in an attempt to obtain compounds suitable for GC. The pectin was deposited from solution on to a platinum spiral and dried until approximately 1 mg of solid had been accumulated. Unfortunately conditions of drying and pyrolysis are rather critical.

The flavour patterns of fruit are very complex, and some workers have concentrated on specific organic classes while others have attempted to elucidate the complete flavour structure. Flavanol glycosides and aglycones have been detected as their TMS derivatives[246] and this analysis has been applied to apple, pear and strawberry. Much work has been carried out in identifying the flavour volatiles of apple and pear, and the work of Gasco *et al.*[247] is particularly important because of the different methods used for concentration and clean-up. In a comparison of methods for measuring apple fruit-volatiles, Knee and Hatfield[248] concluded that passing air over pieces of apple under headspace-trapping conditions gave the most accurate profile of the flavour volatiles.

In an early application of GC in fruit analysis, Meigh[249] studied the evolution of ethylene from

stored apples. Ethylene can be used to stimulate the ripening of fruits and is emitted naturally from apples.

More study has been made of the volatiles of wine than those of grapes but Mattick *et al.*[250] determined the important flavour constituent, methyl anthranilate, in grape juice. The importance of lactones as flavour constituents in fruit was illustrated by Jennings and Sevenants[251] in their analysis of peach. Molina *et al.*[252] made a similar analysis of apricot. 4-(4-Hydroxyphenyl)butan-2-one has been determined specifically in raspberry by Braun and Hieke[253] who suggested that this method could be used to determine the raspberry content of essences and other raspberry products.

The importance of aldehydes as flavour volatiles was illustrated by Forss *et al.*[254] in their analysis of cucumber. They found that the important flavour constituent was nona-2,6-dienal which has the typical flavour of cucumber. Hex-2-enal, non-2-enal and n-hexanal were other aldehydes found. More recently, several alcohols have been discovered in trace amounts, as well as aldehydes.[255]

An example of GC being used to find an unpleasant fruit flavour, is the deduction by Brown[256] that the bitter flavour of unripe avocado was due to C_{17} oxygenated aliphatic compounds.

The main analytical interest in capsicum is capsaicin, which is the pungent principle. Mueller-Stock *et al.*[257] made a study of capsaicin and the related compounds dihydrocapsaicin, nordihydrocapsaicin and *N*-(4-hydroxy-3-methoxybenzyl)nonanamide. The TMS derivatives of these capsicum constituents were separated by Todd *et al.*[258] and the pungencies of the individual compounds were also assessed organoleptically. A GC method utilizing the TMS derivative of capsaicin was found to be more accurate than a spectrophotometric method, for determinations at the 0.5% level in capsicum oleoresins.[258a]

Of all the essential oils prepared from fruits, citrus oils have been most often examined. A popular preseparation before GC is into the terpene hydrocarbon and oxygenated terpene fractions. Ikeda *et al.*[259] examined the hydrocarbon fractions of the oils of lemon, lime, orange and grapefruit. They found that *d*-limonene was the major terpene of lemon, lime and orange oils and confirmed that, generally, monoterpenes form the greatest portion of the total terpene fraction. In oxygenated terpene fraction analysis, Stanley *et al.*[260] separated the aldeydes of lemon, orange and grapefruit oils after clean-up utilizing the formation of aldehyde–Girard T compounds. They found that geranial and neral were the major aldehydes of lemon oil. These aldehydes can be reduced with sodium borohydride to give the corresponding alcohols, which can be determined.[261]

Hunter and Moshonas[262,263] analysed lemon, lime, orange, grapefruit and tangerine oils for alcohols, using glycerol or propylene glycol as the separational solvent, the extract being cleaned up on alumina and subjected to GC–MS analysis.

The problem of deducing quality from the complex array of peaks due to all types of volatiles has been helped by computerization, a good example being the analysis of orange essential oil.[264]

Ikeda *et al.*[265] have also studied the monoterpene composition of several non-citrus essential oils, including bergamot, caraway, nutmeg, cardamom and black pepper.

The analysis of hop oil is particularly important to the brewing industry. Brewing chemists have paid much attention to the quality of hop oil which depends, usually, on the presence of certain compounds in the oxygenated fraction. Roberts[266] found that the important hop-oil constituents were myrcene, farnesene, β-caryophyllene and humulene. He also maintained that esters and ketones were important flavour contributors.[267] More than 120 volatiles have been identified in stored hops by GC–MS.[267a]

Vegetables and their products

Although vegetables have been studied less than fruits, aroma and flavour are important parameters in their quality control and GC has been used to estimate major volatiles and detect off-flavours in stored materials.

One of the first recorded headspace-sampling methods was used by Buttery and Teranishi[268] to measure the compounds responsible for off-flavours in stored potato and carrot. The potato off-flavour described as "baked" was examined by Pareles and Chang,[269] who found that methylpyrazines were the agents responsible.

Various aldehydes and ketones have been found in stored potato crisps by Dornseifer and Powers.[270] Changes occurred in the balance between these flavour volatiles and were related to the state of autoxidation of the oil present in the crisps.

Ayers *et al.*[271] attributed an off-odour of carrots, described as "violets" to β-ionone 5,6-epoxide. The carbonyl volatiles associated with carrot aroma have been determined as their 2,4-dinitrophenylhydrazones.[271a]

It is known that plants of the *solanum* genus contain glycoalkaloids which are potentially toxic, *e.g.*, α-solanine and α-chaconine. The TMS derivatives of these compounds were separated by GC in the analysis of potato tubers, sprouts and leaves.[272]

Geosmin, (*trans*-1,10-dimethyl-*trans*-9-decalol), considered to be one of the characteristic aroma constituents of beetroot, has recently been determined by GC.[272a] The volatiles of cooked artichokes have been removed by steam distillation and analysed by capillary column GC–MS.[272b] The major components found were the terpenes, selinene and caryophyllene.

GC in the analysis of onion, garlic and chive has centred on sulphur-containing volatiles. Brodnitz and Pollock[273] identified nine such compounds in onion oil, mainly di-1-propyl disulphide and other sulphides. Because the EC detector is more sensitive than the FID in its response to di- and trisulphides, a

dual channel system, splitting the GC effluent between both detectors, was used in an examination of garlic oil by Oaks *et al.*[274]

Sulphur-containing volatiles are important flavour constituents of the *cruciferae* genus. Thioglucosides have been determined in cabbage;[275] the interest in them arises from the possibility of their metabolism to simple toxicants, such as thiocyanates. Alkyl isothiocyanates have also been determined in cruciferous vegetables.[275a]

The flavour and aroma volatiles of peas[276] and mushrooms[277] have also been examined.

Some plants or their leaves or roots are pressed to yield essential oils which are employed as flavouring agents. A number of these oils have been extensively analysed by GC.

The peppermint group, which includes rue, pennyroyal and spearmint oils as well as the parent oil, has received considerable attention. Menthol, menthone, menthofuran and eucalyptol have been separated and determined in Yakima Valley peppermint oil by Cieplinski and Averill[278] and by using discriminant analysis, Hartmann and Hawkes[279] successfully identified the geographical origins of 45 different oils. A similar analysis correctly assigned almost all spearmint oils to their sources.[280]

A standard method for the determination of limonene and 1,8-cineole has recently been published.[280a]

A collaborative study of a method put forward for the determination of 1,8-ceneole in various oils, including sage oil, showed that the latter contained between 10.8 and 12.1% of the compound. A similar collaborative study produced a recommended method for the determination of eugenol in bay oil.

Ginger oil has been analysed for flavour volatiles[283] and Clark *et al.*[284] specifically looked for paradols in the oil, considering that the pungency characteristics of these compounds might make them attractive alternatives to capsaicin additives.

A comparison of the distribution of the volatiles of oil of cinnamon from leaf, stem and root was made by Senanayake *et al.*[284a] Altogether 72 compounds were identified and most of them were present in all three oils, but in different proportions.

Coffee, tea and cocoa

Since coffee is of great commercial importance, it is not surprising that a great deal of research has been conducted into the flavour and aroma of different varieties of roasted and unroasted coffees. GC has supplemented the work of the flavour panellist, and with the combination of GC–MS and computerization, most of the compounds responsible for the unique aroma of coffee have been deduced.

Rhoades,[285] in an early paper, described the extraction and separation of 19 volatiles from commercial coffees and found that the ratio of diacetyl to acetylpropionyl increased almost linearly with increase in the roasting temperature.

Quantitative analysis, using a GC–computer system with measurement of peak heights and ratios of volatiles, was used by Biggers *et al.*[286] to differentiate between *Coffea Arabica* and *Coffea robusta*. In one chromatogram there were 404 peaks or inflections, 32 of which were used for discriminant analysis. Sulphur-containing volatiles of the two varieties were separated by temperature-programmed GC and detected with the FPD in the sulphur mode.[286a] There were significant quantitative differences in the amounts of some of the volatiles and these were used to estimate the presence of as little as 1% *Coffea robusta* in *Coffea Arabica*. Volatile phenols,[286b] dihydroxyphenols and furyl derivatives,[286c] and hydrocarbons[286d] have been extracted from and determined in various varieties of coffees.

Tassan and Russell[287] collected the headspace vapours over a coffee brew and entrained the volatiles on a Porapak Q column before GC, then compared the flavour profiles with organoleptic evaluations.

Although caffeine is normally determined by classical methods, the use of a nitrogen-sensitive detector facilitates its estimation in coffee.[288]

Apart from the examination of tea for general flavour volatiles, *e.g.*, the investigation of black tea constituents,[289] GC has been used to determine flavanols in green tea. Pierce *et al.*[290] extracted powdered tea and prepared the TMS derivatives of the flavanols. The derivatives of catechin, epicatechin, epigallocatechin and gallate esters were separated and determined.

Several workers have studied the flavour and aroma composition of roasted and unroasted cocoa beans, not only because of their use as the basis for a beverage but also because the nib portion of the bean is an essential ingredient of chocolate couverture.

Bailey *et al.*[291] examined several cocoa varieties and found that they contained the same volatiles but in differing ratios. They found that aldehydes were very important flavour contributors and their ratios were related to the roasting temperature. A headspace-sampling technique was used for cocoa volatiles by van Praag *et al.*,[292] who confirmed the presence of 56 compounds by GC–MS. A similar sampling technique has recently been used with temperature programmed GC with a stationary phase of Cekachrom (styrene–divinyl benzene copolymer).[292a]

In the last few years the importance of the contribution of pyrazines to flavour and aroma in heat-treated foods has been recognized, and roasted cocoa beans have been analysed accordingly,[293] trimethyl- and tetramethyl-pyrazines being considered the important flavour contributors.

Fogden and Urry[294] differentiated two distinct types of cola drink by GC determination of the caffeine content; one type contained less than 2 mg/l. and the second contained between 70 and 200 mg/l. A similar method was used by Erndt *et al.*[294a]

Beer, wort and cider

The main original criterion for beer was its alcoholic content, but this is now supplemented by consideration of flavour quality. The well-established wet-chemical methods of measuring the ethanol content has given way, in part, to GC methods, which are usually more specific. GC methods have also been used in determining the sugar and amino-acid contents of wort, since these classes of compounds are precursors of some of the flavour volatiles of the beer.

In the determination of ethanol in beer, Trachman[295] used a Porapak Q column in a GSC method and found good agreement with distillation and gravity measurement, but the GC method was faster. Although the presence of methanol in beer is not such a problem as it is in distilled alcoholic beverages, GC gives satisfactory results with samples containing between 0.01 and 0.35% methanol.[296]

Before the advent of GC, it was almost impossible to separate and determine all the sugars present in beer and wort. Clapperton and Holliday,[297] using TMS derivatives, found that the dominant sugar in wort was maltose (2.7–4.8%) with smaller concentrations of fructose, glucose, sucrose and maltotriose. Jamieson[298] converted the sugars of wort or beer into their oximes, before silylation, and this simplified interpretation of the GC results because each reducing sugar gave only one peak instead of one for each anomer present.

Feil and Marinelli[299] determined the glycerol content of lager by direct injection onto the stationary phase Par 1, which is a macroreticular resin. Eleven lagers gave an average value of 1.6 mg/l.

Analysis of the amino-acids in wort can yield valuable information regarding the proteolytic changes as fermentation proceeds and beer is produced. Kurosky and Bars[300] determined the amino-acid contents of beer and wort by using the TFA methyl esters after clean-up on an ion-exchange resin, and in a similar method, Otter and Taylor[301] used the TFA n-butyl esters.

The volatile components in wort and beer, particularly the fusel oils, esters, diketones and sulphur-compounds, have been the subject of considerable investigation, especially by GC. The short-chain fatty acids, *viz.*, C_6–C_{10}, have been determined in wort and beer[302] as have the long-chain fatty acids which can be contributors to the so-called "cardboard" off-flavour.[303] Fusel oil and 2-phenylethanol are important flavour contributors in beer and Morgan[304] has compared the concentrations of these volatiles in stout, pale ale, brown ale and lager. Beers have also been analysed for esters and higher alcohols, with isolation by distillation into a cold trap, a method preferred to headspace analysis.[304a] Engan[305] considered 2-phenylethanol to be the most important aromatic alcohol of beer and found concentrations of between 5.6 and 27 ppm in Norwegian products.

The importance of flavour to the brewing chemist is illustrated by the large amount of analytical literature on the subject, including GC methods in particular. Among the most important papers are some on the determination of diketones,[306–306b] sulphur-containing compounds,[307–308a] phenolic compounds,[309] cetechin[310] and non-2-enal.[311]

An apparatus and procedure for the analysis of a whole range of beer volatiles has been recently described by Williams and Strauss.[312] In this method, headspace sampling precedes flushing onto a trap of Chromosorb 105 and subsequent desorption and GC analysis.

The influence of the flavour constituents of hops on the final beers was studied by Tressl *et al.*[312a] and that of roasted barley by Harding *et al.*[312b]

Kieser *et al.*[313] determined the 2-phenylethanol content of various ciders and Pollard *et al.*[314] determined their fusel oil contents. Subsequently, a whole range of cider flavour constituents was separated and identified by using a concentration technique on Porapak Q and GC–MS.[314a]

Wine and must

The methods used for the determination of ethanol and methanol in beer and wort can be applied to wine or must.

Fixed acids in wine were determined by Brunelle *et al.*,[315] as the TMS derivatives after removal of sugars. Of various fruit wines examined, only grape wine contained tartaric acid.

The fusel oil content of wines of various origins has been determined by Webb and Kepner.[316] They experimented with GC parameters to increase the efficiency of separation of the fusel oil components and found that the major component was always 3-methyl-1-butanol.

The quality of wine depends largely on its flavour and aroma and much work has been carried out on the analysis of the volatile fraction. One of the fundamental problems in analysis of volatiles is their extraction without loss or artefact formation. Hardy and Ramshaw[317] suggested trichlorofluoromethane as extraction solvent since it does not extract water, ethanol or higher alcohols. They used GC–MS to confirm the identities of 41 volatiles in a Riesling wine.

The anthocyanins of red wines have been determined by Drawert and Leupold[318] by use of the TMS derivatives.

Some countries incorporate a tax on carbonated wines and Ashmead *et al.*[319] used GSC on a charcoal column to determine carbon dioxide in wines.

Addeo *et al.*[319a] determined cyanide residues in wine down to the 1-μg/l. level after formation of cyanogen bromide, which was subjected to GSC with EC detection.

Ethylidine glycols are thought to be partly responsible for the characteristic aroma introduced into sherry by the flor process, and these compounds have been estimated together with other volatiles in Australian sherries.[319b]

Brandy

Brandy, being the distilled and matured product of wine, contains the most volatile constituents of wine in addition to newly-formed volatiles. It is to identify these, therefore, that GC is mostly used in brandy analysis.

Methanol is concentrated and formed in the distillation process, and a U.K. Research Committee has recommended three GC methods for the determination of methanol in brandy and other spirits.[320] The methanol content of brandy was shown by Dyer[321] to be between 0.018 and 0.067%.

In addition to exercising control over the methanol content of spirits, the producer should be aware of their fusel oil contents, since these can also reach harmful levels, although the range and balance of low concentrations are essential for the flavour and aroma of the products. Martin *et al.*[322] examined brandy, whisky and rum for fusel oil content and in a similar study Singer and Stiles[323] found that the sum of the concentrations of the C_3–C_5 alcohols could be taken as the total fusel oil content of brandy.

The concept of using the ratios of the fusel oil components as a measure of brandy quality was introduced by Singer;[324,325] he used various ratios of the concentrations of propanol, 2-methyl-1-propanol, 2-butanol, 2-methy-1-butanol and 3-methyl-1-butanol; in a similar approach, brandies imported into Australia have been analysed for the presence of fermented fruit juice other than grape.[326]

A partially successful attempt has been made recently to characterize brands of spirits, including brandy, by using fusel oil analysis.[327]

Esters play an important part in the flavour and aroma of spirits and Guymon and Crowell[328] have related the characteristic brandy flavours to ethyl octanoate, decanoate and dodecanoate. Ethyl acetate and higher alcohols have recently been determined in brandies.[328a]

Whisky and bourbon

The quality of whisky and bourbon, which are grain-based distilled beverages, depends on their flavour and aroma compounds and the same analytical approach can be used as that for fusel oil determination in brandy.[322–325] Hall[329] considered that whiskies could be classified according to the ratio of isopentanol to isobutanol and successfully showed that a whisky labelled as a Scotch blend was in fact a bourbon.

There has been some interest in the analysis of whisky for sugars and glycerol during maturation in newly charred white-oak casks; GC of the TMS derivatives has shown that the glycerol content increased from 0.8 to 2.4 g/l. in a 100° proof whisky.[330]

The differences between malt and grain whiskies are important organoleptically and, therefore, commercially. Duncan and Philp[331] used three different sets of GC conditions to evaluate alcohols, phenols, esters and carbonyls in both types of whisky, in an attempt to produce a method to deduce the proportion of both types in blends. Malt whisky is found to contain a number of alcohols, carbonyl compounds and higher alkanoic acid esters that do not occur in grain whisky; there is a particularly high concentration of 3-methyl-1-butanol (0.16%).

Martin *et al.*[332] specifically looked for ethyl esters of fatty acids and isoamyl acetate in whiskies and rums, in an attempt to relate their concentrations to flavour and aroma character.

More recently, successful attempts have been made to distinguish high-grade and ordinary whiskies by applying statistical and pattern-recognition techniques to the chromatograms of the volatiles.[332a]

Gin

Some of the flavour constituents of gin have been identified by GC–MS by Clutton and Evans.[332b] The terpenes, aldehydes and alcohols detected were consistent with the composition of the essential oils used in gin production, *e.g.*, juniper berry, coriander, cinnamon and cassia.

Rum

Rum, being the distilled product of sugar cane juice or molasses, has a distinctive flavour and aroma. Its fusel oil content has been measured, and often compared with that of brandy or whisky, but a great deal of research has been applied to the satisfactory separation and detection of rum esters. Stevens and Martin[333] considered that the quality of rum was proportional to the concentration of ethyl esters of fatty acids of even carbon number between 8 and 16.

Vinegar

Vinegar, being a fermentation product, is characterized by its volatile constituents as well as its fixed acetic acid. GC has been applied to the determination of volatiles and, in particular, diacetyl and 3-hydroxybutan-2-one.[334] In a general analysis of volatiles, Kahn *et al.*[335] determined alcohols, esters and acids in spirit and cider vinegars.

Sugar and its products

Many sections of the food industry require sugar or sugar syrups as a raw material. The determination of single sugars in foods is relatively straightforward but sugar mixtures often present major analytical problems. The development of TMS derivatives of sugars[336] has resulted in GC often being the method of choice for sugar determination.

There are many methods in the literature for the preparation and separation of the TMS derivatives of sugars, *e.g.*, that of Brobst and Lott[337] for a glucose syrup to be used in the brewing industry. However, most reducing sugars give more than one peak because of the different anomers present. Reduction of the sugars with sodium borohydride to the corresponding alditols, before formation of the TMS deriva-

tives, removes anomerization,[338] but formation of the oximes before alkylation is more convenient.[298] With an open tubular column the TMS derivative of sucrose has been separated in only a minute.[339] A 40 m × 0.5 mm column coated with OV-17 was used. Other sugar derivatives have been used in GC methods, *e.g.*, methyl glycosides,[340] hexa-acetates[341] and TFA derivatives,[342] but TMS derivatives remain the most popular.

Pyrolysis has been little used in the application of GC to food analysis, but the high-frequency pyrolysis of carbohydrates, including glucose, fructose and sucrose, with a Curie-point pyrolyser, was used by Baltes and Schmahl.[342a] The volatile products were subjected to temperature-programmed GC and detected by MS.

Aconitic acid is the predominant organic acid in sugar cane and sorghum cane syrups, and its concentration is important since high levels can cause clarification problems. Johnson and Fernandez-Flores[343] have devised a GC method for aconitic acid as its TMS derivative.

Some interest has been shown by the sugar industry in use of the lactic acid concentration of sugar beet juice and molasses as a direct indicator of microbiological action. Oldfield *et al.*[344] converted lactic acid into acetaldehyde for its GC determination.

Sugars caramelized by heating are used for colouring and flavouring. Sugisawa[345] has identified glucose caramel volatiles and found that acids, aldehydes, alcohols, ketones and furans are the main flavour constituents.

Caramel is produced commercially by the reaction between sugars and ammonia, and there has been some concern that small quantities of substituted imidazoles are formed in the process. A recent GC method for the determination of 4-methylimidazole, the main imidazole contaminant, involves solvent extraction from alkaline solution and results in a detection limit of 0.2 ppm in the caramel.[346]

The U.S. Department of Agriculture has produced a number of GC methods for the detection and determination of volatiles in maple syrup. Among the more important volatiles found are vanillin, syringaldehyde and dihydroconiferyl alcohol. Filipic and Underwood[347] have been responsible for a great deal of the studies.

The main GC analytical interest in honey is the separation and identification of the volatiles. In isolating 120 components from a honey, Cremer and Riedmann[348] considered that the alcohols, ketones, aldehydes and esters found resulted not only from the flowers, but also from the fermentation process.

Cereals and their products

GC has been applied in analysis of the fatty acids that constitute the glycerides of the lipid portion of flour, which can produce up to 4% of the total fat in bread. As early as 1958 Coppock *et al.*[349] examined wheat flour oil; they considered that some of the fatty acids found had an influence on bread aroma and flavour.

Fisher and Broughton[350] have fractionated wheat flour lipids. Linoleic acid (~63%) is the dominant acid in all fractions, followed by palmitic (17–22%) and oleic (9–14%) acid. In an analysis of whole wheat, bran, germ and endosperm for free lipids, Burkwall and Glass[351] also found that linoleic was the major glyceride fatty acid.

Franciosi and Giovannini[352,353] determined the egg content of pastas by analysis of the glyceride fatty acids. Even a small addition of egg significantly reduced the linoleic to oleic acid ratio of the pasta, and other fatty acid ratios were also significantly changed. These workers also indicated differences in fatty acid ratios in hard and mixed wheat pastas.

Various aldehydes and ketones were sought in the volatiles of bread by Hunter and Walden.[354] They used semicarbazide to form derivatives of the carbonyls, regenerating the latter with phosphoric acid for GC determination. Recently, 19 carbonyls and 34 amines have been identified in wheat flour.[355] The volatiles of maize and rice[355a] and of wild rice[355b] have recently been studied by GC methods.

The amino-acid contents of maize and soyabean meal have been determined by GC of the butyl esters of their TFA derivatives, following acid hydrolysis of the proteins.[356] Glutamic acid was the predominant amino-acid found in both products.

GC APPLIED TO ANALYSIS OF ADDITIVES AND CONTAMINANTS

The widespread use of food additives has necessitated the development of organic microanalytical methods, in which GC has played a prominent part. Most countries allow food preservation and the addition to food of antioxidants, emulsifiers, stabilizers, flavourings and artificial sweeteners. Fashion is ever changing and the food manufacturing and legal enforcement analysts have to keep a check on levels of these additives.

Pesticide residue analysis in foods has given great impetus to the use and development of GC techniques in food laboratories. Other contaminants which are determined by GC techniques are PCBs, methylmercury, nitrosamines, solvent residues, food packaging materials, mycotoxins and drug residues.

Preservatives

With the notable exception of sulphur dioxide, most food preservatives can be determined satisfactorily by GC, which has superseded conventional colorimetric methods which, in general, are less sensitive and less specific. GC has been used in the determination of benzoic acid and its hydroxy and halogenated derivatives, dehydroacetic acid, acetic acid derivatives, propionic acid, sorbic acid, salicylic acid, diethyl pyrocarbonate, diphenyl, *o*-phenyl-

phenol, ethylene oxide, nitrous oxide, thiabendazole and imazalil.

Benzoic acid and 4-hydroxybenzoate esters are extensively used as preservatives. Similar methylation methods for the separation and determination of these preservatives were developed by Vogel and Deshusses[357] and by Groebel,[358] the former also separating 2-chlorobenzoic acid, 4-chlorobenzoic acid, dehydroacetic acid, sorbic acid and salicylic acid. Groebel used his method in the analysis of margarine, mayonnaise and meat and fish pastes.

A scheme for the GC determination of 22 preservatives and antioxidants in beer was developed by Silbereisen and Wagner,[359] using methyl derivatives on a capillary column.

Benzoic acid, sorbic acid and the methyl, ethyl and propyl esters of 4-hydroxybenzoic acid have been successfully separated and determined in marmalade, margarine, mustard, mayonnaise, canned fish, beer and wine, by means of the TMS derivatives.[360] Benzoic and sorbic acids have also been determined in fruit juices, syrups and soda-water.[360a]

As little as 5 ng of benzoic acid can be detected in margarine by the simple method of Graveland[361] which merely entails suspending the sample in solvent and analysing the supernatant liquid after centrifugation. A similar method has been used to determine propionic acid and sorbic acid in rye bread.

Fogden *et al.*[362] detected and determined benzoic acid, 4-hydroxybenzoates and sorbic acid in a variety of foods by a GSC method using tris(hydroxymethyl)-methylamine as an additive at the drying stage before the GC, which minimized evaporation losses of the preservatives. A rapid method for the determination of benzoic acid in soft drinks and sugar syrups has recently been published.[362a]

Propionic and sorbic acids were extracted together from bread by steam distillation before solvent extraction and GC determination of the free acids, by Walker *et al.*[363] Nose *et al.*[364] preferred to form the phenacyl ester of propionic acid in their determination of this preservative, using 4-chlorophenacyl bromide as reagent.

Sorbic acid has been determined in prunes down to the 1 mg/kg level by GC–MS of the n-butyl ester.[364a]

Diethyl pyrocarbonate is used as an additive in wine, beer and non-alcoholic beverages to prevent undesirable fermentations. Wunderlich[365] used a method based on the hydrolysis of this preservative to yield ethanol which further reacted with the diethyl pyrocarbonate to give diethyl carbonate which was subsequently determined.

The carcinogen ethyl carbamate can be formed from diethyl pyrocarbonate and ammonia, when the latter is present in a beverage with the preservative. Joe *et al.*[366] used a GC method to determine ethyl carbamate in wine and found between 1 and 20 μg/l.

Biphenyl is normally incorporated in the wrapping papers of oranges and other citrus fruits, to prevent mould growth. *o*-Phenylphenol or its sodium salt is used as a dipping solution for a similar purpose. The usual method of isolation of these preservatives is by steam distillation and solvent extraction of the distillate, followed by GC determination.[367,368] Sweep co-distillation has been used as an isolation technique before the determination of these preservatives, but lemon-peel essential oil ingredients have to be removed with alumina,[368a] whereas the combined steam distillation and solvent extraction procedure incorporated in the Likens–Nickerson apparatus produces a relatively clean extract.[368b] Tanaka *et al.*[368c] used steam distillation isolation and improved the specificity of their method by chromatographing the pentafluorobenzyl derivative of *o*-phenylphenol and using EC detection. Lord *et al.*,[368d] in evaluating methods for the determination of these preservatives in citrus peel, preferred their own GC technique to those specified in certain EEC Recommended Methods.

Biphenyl-impregnated pads used for the packaging of citrus fruits in transportation have been extracted and analysed for the preservative by GC and the results compared with those obtained by HPLC.[369]

Thiabendazole is used in a similar way to biphenyl and *o*-phenylphenol and Mestres *et al.*[370] used a GC method with an FPD used in the sulphur mode for determining down to 0.1 μg of thiabendazole. The methyl derivative[371] and the pentafluorobenzoyl derivative[372] have also been used for GC.

Imazalil has similar properties to thiabendazole and Greenberg and Resnick[373] determined this compound after its solvent extraction and were able to measure down to 0.5 ppm.

In experiments to discover the reaction products of nitrite preservation of meat products, nitrous oxide was evolved thermally and determined by GC on a Porapak Q column.[374] More recently, nitrite and nitrate have been determined in meat products by nitrating added benzene and determining the resulting nitrobenzene,[375] or by nitrating added 2,4-xylenol and determining the resulting 6-nitro-2,4-xylenol.[375a]

Formaldehyde has been used to preserve certain concentrated liquid flavourings, *e.g.*, apple and smoke, and may be determined at the 10 mg/kg level by GC of its 2,4-dinitrophenylhydrazone.[375b]

Antioxidants

GC has been used in the detection and determination of most of the manufactured antioxidants used in food. These include butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), gallate esters, nordihydroguaiaretic acid (NDGA), dilauryl 3,3′-thiodipropionate (DLTDP), 3,3′-thiodipropionic acid (TDPA), 4-hydroxymethyl-2,6-tert-butylphenol (Ionox 100), 2,4,5-trihydroxybutyrophenone (THBP), tert-butylhydroquinone (TBHQ), ethoxyquin, ethyl protocatechuate and guaiac resin.

GC methods have largely replaced colorimetric ones for BHA, BHT and gallate esters. Hartman and Rose,[376] in their determination of BHA and BHT in

vegetable oils, used two different stationary phases to confirm their results. BHA is eluted before BHT on a DC-200 column; the elution is reversed on a Carbowax 20M column.

A vacuum-sublimation clean-up procedure was the feature of a method for the determination of BHA, BHT, propyl gallate, NDGE, DLTDP, TDPA, Ionox 100 and THBP in lard by McCaulley *et al.*[377] These antioxidants were clearly separated on a GE-XE-60 stationary phase.

TMS derivatives of BHA, BHT, propyl gallate, TBHQ and NDGA were used by Stoddard[378] for their determination in vegetable oils. A two-solvent extraction system was used before the GC. If Florisil clean-up was used, BHT could be determined without forming its derivative. Some of the extraction procedures have been improved.[378a]

Heptafluorobutanoyl derivatives of BHA, propyl gallate and TBHQ were separated on an OV-3 stationary phase by Page and Kennedy.[379] EC detection increased the sensitivity of the method. Unfortunately, the BHT derivative is not formed in this method.

Antioxidants are also added to certain vitamin preparations and BHA plus BHT have been determined in vitamin A concentrates.[380]

BHA may be well separated from BHT by use of its TFA derivative.[381]

Ethoxyquin is used as an antioxidant on apples in storage. Winell[382] used the heptafluorobutanoyl derivative of ethoxyquin for GC after extraction of the antioxidant with hexane. With EC detection, down to 0.02 ng of ethoxyquin could be detected.

Citric acid has been used as an antioxidant synergist and can be determined in fats and oils by means of its butyl ester.[383]

Emulsifiers and stabilizers

GC has been used in the determination of emulsifiers and stabilizers which are natural to food, *e.g.*, glycerides, polyglycerides and polysaccharides, and those which have been specifically made to fulfil certain needs, *e.g.*, sorbitan esters and their polyoxyethylene derivatives, brominated vegetable oils, sucrose diacetate hexaisobutyrate and triethyl citrate.

The main problem arising from glyceride and polyglyceride determinations is their separation into groups before GC. The popular technique is column chromatography on silica gel, a good example being given by Sahasrabudhe and Legari[384] who completed the analysis by using the TMS derivatives of mono- and diglycerides. TMS derivatives are most popular in the determination of polyglycerides and Sahasrabudhe[385] applied preparative TLC for their separation before formation of the TMS derivatives of the eight fractions.

An early attempt to determine sorbitan monostearate depended on the presence in the emulsifier of a small concentration of 1,4-3,6-dianhydrosorbitol. This anhydride was determined in cake mixes by Wetterau *et al.*[386] and the sorbitan monostearate concentration was calculated. The TMS derivative of the anhydride has also been used as an indicator of sorbitan ester concentrations in various foods.[387]

Another approach, introduced by Lundquist and Meloan, was the hydrolysis of the sorbitan esters and GC separation of the resulting polyols.[388]

In some countries, brominated vegetable oils (bromine addition products of vegetable oils such as sesame, olive, corn and cotton seed) are used as dispersing agents for the flavouring oils employed in the soft drinks industry.

The GC methods put forward for the separation and determination of brominated vegetable oils have depended on extraction, hydrolysis, methylation and GC determination. In this way, chromatograms are produced which show compounds such as methyl tetrabromostearate, methyl dibromostearate and other methyl esters of fatty acids. By using standard brominated vegetable oils for comparison, Conacher *et al.*[389] were able to deduce which oil had been used in such samples as citrus soft drinks.

Brominated vegetable oils are prohibited in foods in some countries and sucrose diacetate hexaisobutyrate has been used in their place. The most satisfactory method for the determination of this dispersant is through the decyl acetate and decyl isobutyrate formed from it after extraction and treatment with decanol in sulphuric acid.[390]

Triethyl citrate and triacetin are additives used in egg whites to facilitate emulsion and so reduce the time required to produce whipped egg. Kogan and Strezleck[391] ether-extracted these emulsifiers from egg whites in acid medium and determined them on an SE-30 stationary phase.

Polysaccharide gums, such as guar, carob-bean, agar, carrageenan, karaya, methyl cellulose, tragacanth, pectin, acacia and alginate have been detected and, in some cases, determined in foods either by extraction, methylation followed by hydrolysis,[391] or by formation of the TMS derivatives,[392] or through the aldonitrile acetates of the monosaccharides isolated from hydrolysis products.[393,394]

Artificial sweeteners

The addition of artificial sweeteners to food, although long used for reasons of economy because sugar is relatively expensive, has become significant for the reason that they reduce the calorific value when they replace sugar, and weight-conscious populations may benefit. However, the increasing suspicions that not all artificial sweeteners are toxicologically safe have lent weight to their detection and determination in food.

The artificial sweeteners, cyclamates, saccharin, dulcin, sorbitol and the methyl ester of L-aspartyl-L-phenylalanine have been determined by GC methods, which are usually the most sensitive or selective.

The GC determination of cyclamates in soft drinks was pioneered by Rees,[395] using the reaction between cyclamate and nitrous acid to yield cyclohexene

which he measured on an Apiezon L stationary phase. Richardson and Luton,[396] in a modification of this method, used it to determine down to 0.2% sodium cyclamate in soft drinks.

Cyclohexene has also been measured in headspace samples, following the same reaction, and the method has been applied to the analysis of fruit juices, soft drinks, wines and preserves.[397]

The TFA derivative[398] and the heptafluorobutanoyl derivative of cyclamate[399] have also been utilized in its determination.

Cyclohexylamine is the basis of the synthesis of cyclamate and trace amounts are often carried through into the final product and it has been found in various citrus and cola beverages which contained cyclamate. The GC methods depend on either determining the free amine[400] or forming the 2,4-dinitrophenyl derivative, which has strong electron-capturing properties.[401]

Cyclamate often occurs in soft drinks with saccharin, which has been used as an artificial sweetener for over 50 years. Conacher and O'Brien[402] methylated both sweeteners after their solvent extraction and the methyl derivatives were separated on an SE-30 stationary phase.

Koenig[403] separated the methyl esters of cyclamate and saccharin and also free dulcin, which is a sweetener used some time ago but now in only a few countries.

The TMS derivative of saccharin was utilized by Gerstl and Ranfft[404] for its determination in foods, a mixed stationary phase of OV-7 and OV-22 being used.

Toluene-2-sulphonamide is an important trace impurity in saccharin and could be present in detectable amounts in foods to which saccharin has been added. The TMS derivative of this impurity has been used for its GC determination,[405] although the free sulphonamide may also be used.[405a,405b]

A relatively new dipeptide sweetener, the methyl ester of L-aspartyl-L-phenylalanine, has been determined with its degradation products, by GC separation of the TMS derivatives.[406]

When large amounts of sweetener are needed in a dietetic or diabetic food, saccharin and cyclamate are unsuitable because they impart a bitter aftertaste on the palate when used in high concentration. Sorbitol has therefore been used extensively in these special foods and GC determination of the hexa-acetate is common.[407,408] Fernandez-Flores and Blomquist[409] have employed the TMS derivative, finding it particularly useful in the determination of sorbitol in dietetic candies and cakes.

Flavourings

GC has been greatly used in studies of the natural flavourings of many foods, such flavourings being made up of large numbers of components. The analysis of synthetic flavourings can be less difficult since the number of inherent components is ususlly smaller. A great deal of GC analytical work is devoted to the detection and determination of certain flavouring components which could be present and are either known to be toxic or are suspected to be so, *e.g.*, benzaldehyde, coumarin, safrole and its derivatives, methyl salicylate, β-asarone, pulegone and thujone. GC methods have also been used for the determination of ammonium glycyrrhizinate, monosodium glutamate, maltol, ethylmaltol and vanilla.

Benzaldehyde is a major flavour ingredient of cherry and almond flavourings. Brunelle and Martin[410] determined the free aldehyde isolated by steam distillation. They found that natural cherry flavourings contained approximately 0.2% benzaldehyde and that imitations contained up to 2.3%.

Bucci *et al.*[411] have reviewed the public health problems involved in the use of certain flavourings in food and produced a quantitative method for coumarin, detecting as little as 0.2 μg. May wine, a light grape wine flavoured with woodruff herbs, has also been examined for coumarin.[412]

The recommended method of the International Organisation of the Flavour Industry[412a] for the determination of coumarin in foods involves solvent extraction and direct GC.

Liddle and de Smedt[413] used solvent extraction, followed by GC–MS analysis, to look for coumarin, safrole, β-asarone and thujone as flavour agents in vermouth.

Safrole, isosafrole, dihydrosafrole, dihydroanethole and methyl salicylate have been determined in non-alcoholic beverages by Larry,[414] by GC after their isolation by steam distillation and solvent extraction. The International Organisation of the Flavour Industry has recently published similar methods for the determination of safrole and isosafrole in foods and beverages[415] and of α- and β-thujone.[416]

β-Asarone is a component of oil of calamus and this oil has been used as part of the flavouring of vermouth. A steam distillation, solvent extraction and GC method was put forward by Larry[417] for 5–100 ppm levels of β-asarone in vermouth. The recommended method of the International Organisation of the Flavour Industry[417a] for the determination of β-asarone in alcoholic drinks and sugar confectionery involves solvent extraction and direct GC.

β-Asarone, and α- and β-thujone have been determined in aperitifs, including vermouth, by distillation followed by solvent extraction and GC.[418] The limit of detection was 0.01 ppm.

A steam distillation, solvent extraction and GC procedure has recently been recommended as a standard method for the determination of pulegone by the International Organisation of the Flavour Industry in the analysis of confectionery, ice cream, beverages and essential oils.[419]

Ammonium glycyrrizinate can be used as a flavour potentiator in chocolate- and caramel-flavoured beverages. Larry *et al.*[420] have put forward a method for its determination as the TMS derivative, formed after hydrolysis of the sample.

Monosodium glutamate is used primarily as a flavour potentiator in "meaty" food products. Analytical methods usually depend on measurement of glutamic acid and Gal and Schilling[421] have developed a method for its determination as the TFA derivative of the butyl ester. They applied their method to the analysis of soups and seasonings for monosodium glutamate concentrations of between 2 and 17%.

Pesticides

The technology of GC has benefited from analysis for pesticide residues in foods and crops. It is difficult to imagine what would have happened to pesticide residue analysis without the technique, and it was in the late 1950s that GC was given perhaps its biggest advertisement as a microanalytical technique, by the multiresidue analysis of OC insecticides. In this context, the development of the EC detector was all-important,[422] followed by the development of the MC detector.[423] No subject has done more to stimulate detector technology than pesticide residue analysis and by the time analysts became interested in organophosphorus (OP) residues, most of the methods were ready-made, having been developed for organochlorine (OC) residues, except for a specific and sensitive detector; this was to follow in the shape of the AFID.[424]

Because of the persistence and, therefore, accumulation of OC pesticides and their possible hazards to health, many of them have been replaced by alternatives, *e.g.*, carbamates and, therefore, GC has been applied increasingly to these and other organonitrogen (ON) pesticides.

Thousands of papers have been published concerning the application of GC to pesticide residue analysis and it is only possible in this review to include some of the more important contributions.

Organohalogen pesticides. The concern shown internationally about the persistence of OC insecticide residues and their ecological effects has led to numerous surveys of such residues in virtually all types of food. Once the detector systems had been established, the largest variations in published methods were in the extraction and clean-up of the residues.

The initial extraction is mainly done with acetone, hexane or petrol, acetonitrile, dimethylformamide, dimethylsulphoxide and propylene carbonate. Clean-up of samples is usually done by solvent partition followed by column chromatography on Florisil, alumina or activated carbon.

In 1960, Goodwin *et al.*[425] applied GC to the detection of aldrin, dieldrin, *pp'*-DDT and γ-BHC at the 0.05-ppm level in crop extracts, a method later improved upon by a change from argon ionization detection to EC.[426]

Acetone extraction, followed by addition of sodium sulphate solution and extraction of OC compounds into petrol, was used by Hamence *et al.*[427] in the examination of food samples. For clean-up they used further partition into acetonitrile, addition of sodium sulphate solution to the acetonitrile extract and re-extraction into petrol.

The direct extraction of food samples with acetonitrile, thus omitting acetone, is the main difference in the American procedure, *e.g.*, in the official AOAC method. The method is used for the analysis of residues of both OC and OP pesticides. The sample, blended with acetonitrile, is extracted with petrol after the addition of water, and the petrol extract is cleaned up on Florisil, mixtures of petrol and diethyl ether being used for elution. The stationary phase used is 10% DC-200 and detection is by EC for OC compounds. This official method was based on the original work of Burke and Giuffrida.[429]

Although little work had been carried out until the 1970s on combining GC with MS detection in residue analysis, the fact that PCBs can be co-extracted with OC pesticides created interest. Bellman and Barry used GC–MS to examine foods for both species.[430]

Luckas *et al.*,[430a] in a method involving the determination of DDT and TDE by means of reaction with MgO to produce alkenes for GC, were able to separate these OC insecticides from PCBs, which did not react.

A useful identification method for use before GC of OC pesticide residues depends on the partition of the compounds between two immiscible solvents, such as hexane and acetonitrile. Beroza and Bowman[431] used this technique by determining the characteristic degree of extraction (%) of individual OC pesticides when equal volumes of the two phases were used, and applied the values for analysis of crop residues; the co-extractives did not affect the degree of extraction.

In 1965, Storherr and Watts[432] introduced the clean-up method termed sweep co-distillation as part of the determination of both OC and OP pesticides. These workers noticed that crop extractives not removed by hitherto standard clean-up procedures were deposited on the glass-wool packing at the injection end of the GC column. Taking advantage of this, they produced a heated pre-column of glass wool, complete with injection port and carrier gas inlet. Large volumes of pesticide extracts were introduced into the heated tube and the pesticides were swept from it by nitrogen into a cooling coil, before GC. The portion of glass wool containing the co-extractives was periodically replaced. The technique has been found particularly useful in the analysis of fatty foods and many variations on the original technique have been used, *e.g.*, a silanized glass bead pre-column in place of the glass wool.[433]

In an effort to simplify the clean-up procedure, Telling *et al.*[434] have recently used acetone–hexane as extractant and a single alumina column for clean-up, with hexane as eluent.

Fumigants are used extensively for the control of insects and moulds in stored foods such as grain or flour, and many of these are simple halogen-contain-

ing aliphatic compounds which are amenable to GC separation and determination.

Bielorai and Alumot[435] used a GC method for determining the fumigants chloroform, carbon tetrachloride, trichloroethylene and carbon disulphide in cereal grain, with a steam-distillation step incorporating toluene as co-distilling solvent.

Ragelis *et al.*[436] extracted wheat flour and ground pepper by percolating diethyl ether through a column of the sample, in a method to determine chlorohydrins resulting from fumigation of stored food with ethylene and propylene oxides. The compounds 2-chloroethanol and 1-chloro-2-propanol were directly determined in the percolate from the wheat flour, and after clean-up on Florisil, in the percolate from the ground pepper.

Ethylene dibromide, methyl bromide and also 2-chloroethanol from ethylene oxide were determined in flour and grain by Heuser and Skidmore.[437] The samples was extracted with aqueous acetone, and after settling the supernatant liquid was examined by GC.

The most widely applied halogen-containing fungicides are the chlorinated benzenes. Di Muccio *et al.*[438] successfully separated the α-, β-, γ-, and δ-isomers of BHC and hexachlorobenzene, the feature of the GC being the mixed stationary phase comprising 3% OV-61, 7.5% QF-1 and 3% XE-60, (2:2:1 v/v), which is necessary to separate these compounds, which have short retention times on most phases.

Residues of the well-known organochlorine herbicides, 2,4-D, 2,4,5-T, MCPA and MCPB have been successfully determined by GC after methylation[439] or silylation.[440]

Organophosphorus pesticides. The OP pesticides are almost exclusively insecticides and acaricides. Much of the experience gained in the extraction and clean-up of OC pesticide residues has been applied to OP pesticide residues, which has saved time in method formulation. Solvents used for extraction include chloroform, dichloromethane, ethyl acetate, methanol, benzene, hexane and propylene carbonate, whereas the column chromatographic materials used in the clean-up procedures are the same as those used in OC pesticide residue analysis.

Detectors sensitive to phosphorus have been used to advantage, *viz.* the AFID, FPD and the plasma detector; the MCD has been used in the determination of sulphur-containing OP compounds.

The sweep co-distillation clean-up technique used for OC pesticide residues has also been used for OP pesticide residues[432] and, with initial ethyl acetate extraction of food samples, this technique has been incorporated into the Official Methods of Analysis of the AOAC.[428]

Bowman *et al.* analysed 39 foods for multiresidues of pesticides containing phosphorus and/or sulphur.[441] Four extraction procedures were used, depending on the nature of the food. OV-101 and OV-210 were the stationary phases used and detection was by FPD in both the phosphorus- and sulphur-sensing modes.

The choice of clean-up procedure and detector in the GC of OP pesticide residues has overshadowed other factors in the analysis. Many stationary phases are suitable for single OP compounds, but the choice of a phase to separate and determine large numbers of OP compounds is limited. Bowman and Beroza[442,443] tabulated the retention data of 138 pesticides on OV-101, OV-17, OV-210 and OV-225 as stationary phases and 146 pesticides on Dexsil 300.

Various methods were recently examined in a collaborative study for the analysis of residues of common OP pesticides, including malathion, dichlorvos, dimethoate, omethoate, parathion and azinphos methyl,[444] and certain procedures were recommended; guidance on the preparation of GC columns was also given.

Residues of thioether OP pesticides, *e.g.*, carbophenothion and demeton, have been determined in fruits and vegetables after oxidation by permanganate to the corresponding *S,S*-dioxides.[444a]

MS was used as detector in a recent GC method for the determination of 23 OP pesticides liable to be present in fruits and vegetables.[445] Ten pesticides were determined at the 40-ppM (parts per milliard) level, by fragment measurement with single- and multiple-ion detection.

Organonitrogen pesticides. Organonitrogen (ON) pesticides include carbamates, substituted ureas, thiocarbamates, triazines, substituted phthalimides and cyano- and nitro-phenols.

The detection and determination of sub-ppm levels of multiresidues of ON pesticides has lagged behind those of OC and OP pesticide analysis. Discouragement of the use of DDT and other OC pesticides has enhanced the use of carbamates, especially carbaryl.

Martin's detector,[446] which incorporates a furnace in which the nitrogen released from the compound is reduced to ammonia and titrated coulometrically, is an example of detection methods developed for ON compounds.

Coulson[447] used his electrolytic conductivity detector after reductive pyrolysis of ON compounds with a nickel-wire catalyst. A method incorporating this type of detector system has recently been evaluated for 15 ON pesticides, including carbamates and triazines.[448]

Examples of use of derivatives for the estimation of carbamate pesticide residues include 2,4-dinitroaniline derivatives[449] and on-column trans-esterification.[77]

For its GC determination, carbaryl has been converted into its *N*-methylthio derivative, with methylsulphenyl chloride.[449a]

Thiocarbamates are largely used as fungicides, and in 1971 Onley and Yip[450] applied a GC method to the determination of ethylene thiourea residues. Ethylene thiourea is a degradation product of thiocarbamate and although its determination gives neither a specific nor quantitative estimation of the former presence of thiocarbamates, it is a very good indicator of

it. Many procedures are based on the same general idea. The pentafluorobenzoyl derivative of ethylene thiourea was used by Newsome[450a] for its GC determination in vegetables, down to 20 μg/kg.

The triazines used are almost all herbicides. As early as 1962, 6 triazines were separated and determined,[451] and later 9 triazines from crops were extracted, cleaned up and determined by Delley *et al.*[452]

The important substituted phthalimides, namely captan, captafol and folpet, are foliar fungicides. Baker and Flaherty[453] extracted and cleaned up residues of these fungicides from samples of fruit and, after chemical separation techniques, determined all three compounds by GC.

Pyrethrins. Pyrethrin compounds are used extensively as insecticides and of several GC methods that by Bevenue *et al.*[454] is recommended.

Paraquat and diquat. Paraquat may be determined in residues on crops by acid-extraction, hydrogenation and clean-up by column chromatography on alumina, before GC separation and determination with an AFID.[455] Diquat in potatoes may be determined by extraction, reduction with $NaBH_4$ to yield a diamine derivative, and GC with a nitrogen-selective detector.[455a]

Phosphine. This is used as an insecticidal fumigant in wheat. Direct headspace sampling has been used,[455b] and so has gas sampling after the wheat has been extracted with dilute sulphuric acid.[455c]

Polychlorinated biphenyls. PCBs show plasticizing and dielectric properties and have been used in the manufacture of paints, rubbers, resins, lubricants and dielectric fluids of capacitors and transformers. Like OC pesticides, they are fat-soluble and persistent, and have found their way into animals and animal products which may be used for human consumption, *viz.* fish, eggs and game birds. Because PCBs are structurally similar to OC pesticides, much of the analytical literature concerning PCBs deals with their separation from OC pesticides, before GC determination, usually with EC detection.

In 1967, Holmes *et al.*[456] pointed out that analysts had long been aware that some bird and fish samples produced additional peaks in standard OC pesticide residue analysis and that some of these, at least, were probably due to co-extracted PCBs. Jensen[457] had earlier emphasised the presence of PCBs in conjunction with OC pesticide residues.

Risebrough *et al.*[458] found that the chromatograms resulting from the examination of bird and fish samples exhibited mutual interference by DDT-type insecticides and PCBs. It was possible to hydrolyse DDT and its metabolites with ethanolic potassium hydroxide and record the removal of the signals due to these compounds.

Another method of dealing with the interference is to irradiate the GC effluent with ultraviolet light to degrade the PCBs and then to re-chromatograph the degradation products.[459]

PCBs can also be degraded by reaction with a palladium catalyst. Asai *et al.*[460] applied this technique to 8 PCB mixtures and to members of the DDT family. The degradation, which can produce hydrogenation, dehydrogenation and hydrogenolysis, results in biphenyl and cyclohexylbenzene from PCBs, and different products from the DDT family.

There is some concern regarding the presence of toxic polychlorinated dibenzodioxins in PCBs and these compounds have been separated and determined by GC–MS from samples of Yusho oil.[461]

Methylmercury. Mercury compounds have found their way into waterways as a result of the depositing of mercury-containing industrial effluents, and through the leaching of organomercurial fungicides from soil. Fish and other aquatic life can accumulate mercury residues, most of which is converted into methylmercury, and this has a relatively high mammalian toxicity.

Much of the earlier GC work on methylmercury in such foods as fish, meat and eggs, was due to Westoo.[462,463] These methods were based on benzene extraction of the acidified sample and clean-up of the extract, and finally chromatography of methylmercuric chloride. A step was later introduced to split methylmercury from certain natural sulphur compounds with which it can be complexed.

An atomic-absorption spectrometric detector was used by Gonzales and Ross[464] in GC studies on alkylmercury-containing effluents and fish. The methylmercuric halide was separated on the column and determined by flame or flameless atomic-absorption. The microwave-powered plasma detector has been used specifically for the determination of methylmercury in fish samples.[54]

Inorganic mercury compounds have been converted into methylmercuric halides for subsequent GC determination by using such reagents as 4,4-dimethyl-4-silapentane-1-sulphonate[465] and tetramethyltin.[466]

N-*Nitrosamines.* *N*-Nitrosamines may be formed by reaction between secondary amines and nitrous acid. It is well established that some of the nitrosamines, particularly nitrosodimethylamine, have hepatotoxic and carcinogenic properties, and there has been some concern about the finding of trace amounts of nitrosamines in such foods as fish, meat, bacon and cheese. Many analytical techniques have been employed for their detection and determination but there is general agreement among analysts that the only foolproof technique is GC coupled to MS. Hence some results published before 1970 should be treated with caution since MS was not in general use for that purpose before that date.

Gough[466a] has reviewed the determination, by GC-MS, of those *N*-nitroso compounds which may occur in such foods as bacon, fish and cheese.

Gough and Webb,[467,468] described a membrane separator which is capable of transferring nanogram quantities of nitrosamines from the GC column to the

mass spectrometer, a detection limit corresponding to 1 μg of nitrosamine per kg of food being obtained. This GC–MS method was used successfully by Crosby *et al.*[469] in the confirmatory determination of steam-volatile nitrosamines in bacon, fish, meat and cheese samples, which was a development of an earlier method.[470]

Telling *et al.*[471] determined five volatile nitrosamines in meat products, *e.g.*, pork luncheon meat, using a GC–MS method which was subsequently made more sensitive[472] by monitoring ions other than NO^+ (which was first used). Fish was examined for nitrosamines by Fazio *et al.*,[473] nitrosodimethylamine (4–26 μg/kg) being found in sable, salmon and shad. A sample of ham was found to contain 5 μg of nitrosodimethylamine per kg by the same method.[474] Recent results for nitrosamines in meat products include nitrosopyrrolidone in fried bacon samples, in the range 5–75 μg/kg,[474a] and its 3-hydroxy derivative in fried bacon and sausage, in the range 1–10 μg/kg[474b] and also in fried bacon and its "fried-out" fat, in the range 0.3–3.9 μg/kg.[474c]

Nitrosamines in foods have also been determined as their heptafluorobutanoyl derivatives by EC detection[475] and also after oxidation to the corresponding nitramines.[476]

Pokrovskii *et al.*[476a,476b] converted nitrosamines into their dansylamides, by means of secondary amines, and chromatographed these derivatives, using MS detection.

Methylguanidine is considered to be a precursor of nitrosamines in fresh beef and certain varieties of fish, and a GC method for its determination has recently been published.[477]

Solvents. Solvents such as ethanol and 2-propanol are used for incorporation into foods of such additives as flavourings, essential oils, colourings and antioxidants. Solvents such as hexane and acetone are used in the food industry to remove fats and oils, and aliphatic chlorinated hydrocarbons are also used to remove caffeine from coffee. As a result of these practices, there is a possibility that trace solvent residues may remain in the foods and GC is ideally suited to their detection and determination.

Aliphatic hydrocarbons and acetone. In an attempt to determine a number of solvent residues liable to be encountered in oils and spice oleoresins, Dean *et al.*[478] used a solid sampling device to avoid a clean-up procedure. The sample was introduced into a glass capillary which was sealed and enclosed in the sampler, which was then connected to the GC column and brought to equilibrium temperature; the glass capillary was broken by a plunger and the volatile solvents were swept into the column by the carrier gas. The method can be used for different classes of solvents by using different stationary phases and examples of the determination of hexane and trichloroethylene in vegetable oils were given.

Hexane is the most common residue found in edible oils or their associated meals or flours. Soyabean and cottonseed meals and flours were examined for hexane and acetone residues by Fore and Dupuy,[479] by solvent extraction followed by GSC. The same workers have used a headspace-sampling technique,[480] which was subsequently modified by using a glass injection port liner in place of a serum bottle as the sample container.[481] Further improvement in headspace sampling has recently been claimed.[482]

Hop extract, used as a brewing additive, can contain residual hexane, and Litchman *et al.*[483] used headspace sampling and GSC, achieving a detection limit below 25 ppm.

Hirayama and Imai,[484] in the determination of hexane in edible oils, pyrolysed samples in a platinum boat inserted into the pyrolyser, in order to free the solvent from the oil.

Besides hexane residues in oil samples, 2-methylpentane, 3-methylpentane and methyl cyclopentane have also been determined.[485]

Headspace sampling has been used for the determination of acetone in oilseed meals and flours.[10]

Chlorinated hydrocarbons. Roberts[486] conducted a collaborative study on the GSC determination of dichloromethane, ethylene dichloride and trichloroethylene in oleoresins of paprika, ginger and capsicum after their extraction with ethanol. By using vacuum distillation extraction technique with toluene as carrier, Page and Kennedy[487] have improved this analysis.

Dichloromethane is a popular solvent for decaffeinating coffee and Gal and Schilling[488] used steam-distillation and GSC for its determination. Page and Charbonneau[489] improved the extraction technique by using their co-distillation method in the determination of dichloromethane and trichloroethylene residues in instant and roasted coffees.

Methanol and 2-propanol. Methanol is sometimes used in the production of hop extract additives for the brewing industry, and Litchman and Upton[490] devised a GC method based on the reaction of methanol with nitrite and measurement of the product after headspace collection.

2-Propanol has been used to detoxify mould damage in oilseed meals and flours, and a headspace technique has been used for its collection before GSC determination.[9] 2-Propanol has also been used for dewaxing apple peel, and a headspace technique has been used to collect it.[491]

Food packaging materials

There has been increasing interest in the migration of food packaging materials and their additives into foods, particularly those foods containing oil or fat, which are good solvents for these materials. The earlier GC analytical literature was almost exclusively German and concerned the migration of phthalate plasticizers. The more recent literature is concerned with the migration of vinyl chloride monomer from

poly(vinyl chloride) containers into beverages and vinegar.

Phthalate esters. Phthalate esters are used as plasticizers in a variety of food packagings and solvation by fatty or alcoholic foods or beverages can lead to the uptake of these esters.

In 1963, Wandel and Tengler[492] investigated the possible transfer of diethyl phthalate from plastic wrappings into fat-containing foods, using solvent extraction and a GC method with a detection limit of 2 ppm. The same workers[493] also devised a method for the determination of bis-(2-ethylhexyl) phthalate and tributyl *O*-acetyl citrate by means of corresponding alcohols, produced by hydrolysis. A similar method was used by Pfab[494] in migration studies of dibutyl phthalate and dicyclohexyl phthalate from lacquered foil into cheese and lard.

Because of the wide use of phthalate plasticizers, there has been concern that oceans and other waterways may become contaminated and that fish may accumulate these esters. Accordingly, dibutyl phthalate and bis-(2-ethylhexyl) phthalate have been sought in fish.[495]

Vinyl chloride. Vinyl chloride monomer can be present at the ppm level in poly(vinyl chloride) used for food packaging. Because it is alcohol- and fat-soluble, alcoholic beverages and fatty foods packaged in poly(vinyl chloride) are prone to dissolve any monomer present in the container.

Williams and Miles[496] determined vinyl chloride in alcoholic beverages, vinegar and peanut oil by headspace collection followed by GSC. The presence of vinyl chloride can be confirmed by conversion into 1,2-dibromo-1-chloroethane and detection by EC.[497] A solvent extraction method was used for vinyl chloride by Ernest and van Leirop,[498] who used an electrolytic conductivity micro detector, the vinyl chloride having been converted into hydrogen chloride. The method could detect 4 ng of vinyl chloride. A headspace collection of vinyl chloride followed by GC–MS determination has been successfully used in recovery studies on olive oil.[499] The method is also claimed to be suitable for the analysis of wine, soft drinks and margarine. A detection limit of 1 ppm has recently been obtained in a headspace–GC method for vinyl chloride in corn oil.[500]

Styrene. Polystyrene used for food packaging often contains small amounts of styrene momomer, which is fat-soluble. Roseli and Marek[501] recently determined styrene monomer in yogurt, cream and curds by a GC method after solvent extraction.

Acrylonitrile. Polymers containing acrylonitrile are used extensively in the manufacture of containers for carbonated beverages and other foods, such as luncheon meat, margarine and vegetable oils. Since the small fraction of unreacted monomer in the polymer can migrate into the food, GC methods have recently been used to detect it, either by direct injection[501a] or by headspace sampling for carbonated beverages after decarbonation.[501b] By the latter method, traces (less than 5 μg/kg) of acrylonitrile were found in some samples of beers and soft drinks.

Mycotoxins

GC has been applied to the determination of the following mycotoxins resulting from mouldy or damaged foods.

Patulin. Patulin is a carcinogenic, mutagenic metabolite produced by certain strains of penicillin. Since storage rot in apples is caused by a similar penicillin to that known to produce patulin, there is a possibility that the mycotoxin could be transmitted to the juice, cider or cider vinegar. The presence of patulin in apple juice has been tested for by means of the trichloroacetate derivative,[502] and in cider vinegar by means of its acetate.[503] Rosen and Pareles[504] determined patulin as its TMS derivative and this method was applied to the analysis of cereals and rice.[505]

Penicillic acid. Penicillic acid is a mycotoxin which has been proved to be a carcinogen in rats. It is formed from certain species of *penicillium* and *aspergillus*. The TMS derivative can be used in its GC determination in cereals,[505] rice,[505] and maize, dried beans and apple juice:[506]

Sterigmatocystin. Sterigmatocystin is a secondary metabolite produced by several *aspergillus* species and has exhibited hepatotoxic effects. This toxin has been extracted from and determined in grain, with a detection limit of 20 ng.[507]

Trichothecenes. Mouldy grain can yield trichothecenes, which are fungal metabolites found in grain. Ikediobi *et al.*[508] used solvent extraction and GC of the TMS derivatives of those trichothecenes which contain free hydroxyl groups. A similar method was used for trichothecenes in maize and freeze-dried potato powder.[508a]

Ipomeamarone. Ipomeamarone is a hepatotoxin produced by fungal attack of sweet potato. Boyd and Wilson[509] extracted the mycotoxin from samples of sweet potato by homogenizing with 5% methanol in chloroform, and determined the concentration by GC. A similar method was used by Wood and Huang.[510]

Diethylstilboestrol. This is a synthetic oestrogen used as an animal feed additive to increase the feeding efficiency in cattle and lambs. This hormone has carcinogenic properties and residues have been found in tissues of animals treated with it, with concentration in the liver and kidneys. Coffin and Pilon[511] described a GC method for the determination of diethylstilboestrol in beef, lamb and chicken tissues, which involved solvent extraction, clean-up and chromatography of the TFA derivative. Other derivatives used in similar methods include the TMS derivative[512] and the dichloroacetate.[513] Ryan and Pilon,[514] in an analysis of beef liver, made the TFA derivative and, after hydrolysis to yield the free sterol, prepared the heptafluorobutanoyl derivative. With EC detection, the sensitivity was better by a factor of 4 than that for the TFA derivative.

The synthetic steroid melengestrol has also been determined in beef tissues by GC.[515]

Chlorophenols

Chlorophenols are used as wood preservatives, and shavings of the treated timber have been used as litter in broiler poultry houses. Pentachlorophenol and 2,3,4,6-tetrachlorophenol can permeate the chickens and the flesh has been analysed for these compounds, as the 2,4-dinitrophenyl ether derivatives, by GC.[516] Milk has been tested for pentachlorophenol residues by chromatographing either the acetate[516a] or the methyl derivative[516b] after solvent extraction. Broiler chickens have also been found to accumulate 6-chloro-*o*-cresol from cresylic acid disinfectant, and the tainted flesh has been analysed by GC–MS.[517] Griffiths and Land[518] determined the same cresol in biscuits contaminated with a similar disinfectant.

CONCLUSIONS

GC has been of inestimable value in the detection and determination of the organic constituents of food, those organic compounds deliberately added to food and those accidentally contaminating it. But what influence has food analysis had on GC and where do future technology and applications lie?

The three areas of GC technology where food analysis has had greatest impact are sampling, derivative formation and detection.

In sampling, foods which require qualitative and quantitative assessment of volatiles have lent themselves to experimentation which has aided the chromatographer in other applied fields; headspace sampling, preconcentration techniques on solid adsorbents and post-column removal of relatively large concentrations of interfering compounds before separation of minor ones, are examples.

The fatty-acid composition of the glycerides which make up edible fats and oils has frequently been the driving force behind the development of alkylation techniques, particularly methylation. In halogeno-esterification, sterols extracted from foods have been the media for development of methods in which EC detection has enhanced sensitivity.

The silylation of sugars was a major breakthrough in the analysis of sugar mixtures and most sugar-containing foods have been used as bases for enhancing the knowledge of silylation techniques.

Detector technology owes a great deal to the impetus afforded by the necessity to determine groups of pesticide residues in crops and foods, *e.g.*, the use of the EC detector, AFID, FPD and MCD, in the analysis of OC, OP and ON pesticide residues. It is probably in the advancement of detector technology that food contaminant analysis has had greatest impact.

As analytical requirements become more detailed, the demand will be for greater sensitivity and selectivity. This is particularly relevant in the analysis of food volatiles where quality assurance and trades description requirements combine to demand determination of hundreds of minor constituents. In this area, the greater availability of MS, the application of pattern-recognition techniques and the increasing use of microprocessors will mean more detailed examination of a variety of foods and additives, *e.g.*, beverages, essential oils and food flavours.

The uncertainties and vagaries of biological detectors, *e.g.*, moths and the human nose, have resulted in little use of these. Yet food analysis could clearly benefit from use of sniffing of separated components concurrently with MS and the other conventional detection methods.

The microprocessor revolution could also mean a greater use of pyrolysis techniques in GC applications in food analysis, where one drawback has been the difficulties in separating and relating pyrolysis products to the foreign compounds sought within an array of compounds derived from the food matrices.

Although large areas of food quality-control methods suitable for GC application have been exploited, there remains scope in pattern-recognition analyses, particularly for flavour constituents and other volatiles of butter, cheese, animal fats, meat flavours, fruits, vegetables and essential oils.

Fine differences in the ratios of glyceride fatty acids of edible oils continue to be the subject of considerable research as does the balance of volatiles in both alcoholic and non-alcoholic beverages to assess quality and origin.

As new additives are put forward for use, analytical methods are required and GC is often applicable. Changes occur from time to time in permitted lists of preservatives, antioxidants, emulsifiers, stabilizers, artificial sweeteners and flavouring agents and trends in concentrations are usually downward, requiring more sensitive methods.

Similarly, as new contaminants are encountered, the food analyst usually has to add to his repertoire of GC methods. Technology in food packaging is changing and very sensitive methods are required for the determination of compounds associated with migration of contaminants from packaging materials into foods; low levels of monomers are contained in polymeric packaging materials and have been known to migrate into foods.

The large increase in the use of drugs and other pharmaceuticals in animal husbandry has alerted analysts to seek residues of these substances in such foods as milk and meat. New pharmaceuticals are frequently being introduced in veterinary practice and relevant analytical methods are subsequently required.

In conclusion, there is no evidence to suggest any reduction in the activities of the food analyst with GC applications. New compounds requiring analysis will be incorporated into existing systems, which will continue to undergo advantageous changes in data-processing, resulting in increased sensitivity and selectivity.

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EFFECT OF HYDROGEN-ION CONCENTRATION ON THE EXTRACTION OF COBALT, NICKEL, CADMIUM AND LEAD WITH APDC/MIBK: TIME STABILITY OF THE EXTRACTS

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Summary—The extraction of cobalt, nickel, cadmium and lead ions by means of APDC/MIBK has been studied at various acidities of the aqueous phase (pH 0.2–6). Lead and nickel are extracted equally well over this pH-range, while cobalt and cadmium require pH > 1. The time stability of the extracted complexes in MIBK increases in the order cadmium < lead < nickel < cobalt. The decomposition of the complexing agent or the metal complexes is rapid in the two-phase system MIBK/water.

Several investigators have used the diethyldithiocarbamate (DDC) or the tetramethylenedithiocarbamate ion (commonly called pyrrolidinedithiocarbamate, PDC) as chelating agents in the determination of various heavy metals in trace amounts. The complexed metal ions are extracted into an organic solvent and determined by atomic-absorption spectrophotometry *etc.*

The extraction of the metal complex into the organic phase depends upon the hydrogen-ion concentration of the aqueous phase. With other experimental parameters kept constant, the amount of the metal ion extracted will decrease steeply if the pH is less than some critical value. Thus, pH-control is necessary for complexation and extraction. Many analytical procedures require precise (±0.1 unit) adjustment of pH, usually in the range 2–4. However, some studies indicate that the pH-range for quantitative extraction with PDC is fairly wide for lead, (the pH interval is given as 0.1–6,[1] or 0.25–8,[2]) and cobalt (pH 1–10,[3]), but more restricted for cadmium (pH 1–4,[3]). The pH interval suitable for nickel has been given as 2–4[1] and 3.5–8.[4] Extraction *vs.* pH data are presented here for these four metal ions, supplementing the earlier data.

The chelating agents mentioned above are unstable in acidic aqueous solution. The decomposition proceeds through the dithiocarbamic acid, according to the scheme:[5]

$$R_2NCS_2^- + 2H^+ \rightleftharpoons R_2NCS_2H + H^+ \rightleftharpoons R_2NH_2^+ + CS_2 \quad (1)$$

The decomposition is favoured when the pH of the solution is less than the pK_a value of the $R_2NH_2^+$ ion. The half-life for decomposition, $t_{1/2}$, will be independent of pH when the pH is much less than the pK_a value of the dithiocarbamic acid ($pK_a \sim 4$ for HDDC, $pK_a \sim 3$ for HPDC).[5] The half-life is reported to be of the order of seconds for HDDC[2,6] and 25–32 min for HPDC[2,6] under acidic conditions.

PDC is often preferred to DDC when extractions are performed in acidic solution. Contradictory reports have appeared concerning the usefulness of DDC for extractions in the pH-range 2–4.[7,8]

From a practical point of view, the decomposition of pure dithiocarbamic acid in aqueous solution is not so important as the time stability of the various metal complexes after extraction into an organic solvent, e.g., methyl isobutyl ketone (MIBK). Several reports[2–4,9–14] have commented on the limited time stability of PDC-complexes in MIBK, but a more precise comparison of the various values reported is difficult, owing to differences in experimental conditions. It is clear, however, that the time stability is different for different metal ions. The manganese–PDC extract in MIBK seems to be unstable,[12] but the cobalt complex has good stability.[4] The lead and nickel extracts are said to be stable for 5 and 3 hr, respectively,[4] and the nickel extract for more than 15–20 hr.[14] The cadmium complex is said to be stable for more than 72 hr,[11] but very easily decomposed during the extraction step.[13]

Some difficulties encountered in our laboratory seemed to be caused by decomposition of the MIBK extracts and we have, therefore, investigated the stability of the ligand in water/MIBK mixtures. We have also studied the variation in time stability of cobalt, nickel, cadmium and lead tetramethylenedithiocarbamate complexes in methyl isobutyl ketone with the pH of the aqueous phase and the contact area between the MIBK and aqueous phases.

EXPERIMENTAL

Apparatus

A Perkin–Elmer 403 atomic-absorption spectrophotometer with a 10-cm single slot burner was used and was operated as recommended by the manufacturer.

Procedures

To 100 ml of demineralized water were added a suitable amount of the metal ion (0.1 μmole of Cd, 1 μmole of Ni or Pb, 2 μmole of Co), 5 ml of 20% ascorbic acid solution and 5 ml of 1% ammonium PDC solution. Ascorbic acid was added to imitate the conditions of analysis of some samples at this laboratory (it is used to diminish the interference from iron). After adjustment of pH, by addition of hydrochloric acid or ammonia solution, the solution was transferred to a 200-ml standard flask and extracted with 20.0 ml of MIBK by vigorous shaking for 1 min. The organic phase was raised into the neck of the flask by addition of an aqueous solution with the same pH value as the aqueous phase.

The time stability of the extracts was studied under various conditions. In some experiments, the MIBK phases were separated from the extracted aqueous phase, transferred to test-tubes and stored, without water present, or with 5 ml of demineralized water. In other experiments, the MIBK was kept in contact with the extracted aqueous phase. The aqueous phase was stirred with a magnetic stirrer either very gently (*ca.* 120 r.p.m.) or more vigorously.

The stability of the cadmium complexes in MIBK solution in contact with the extracted aqueous phase was studied at different acidities with the aqueous phase either unstirred or stirred very slowly.

The absorbances of "aged" samples were compared with those of freshly prepared standards. The experiments were duplicated and average values are given in the tables. The absorbances are accurate to ±3%.

The rate of decomposition of pyrrolidinedithiocarbamic acid, HPDC, was measured by taking samples at various time intervals and analysing for PDC by addition of copper chloride solution in excess and spectrophotometric determination of the copper complex, extracted into chloroform.[15] The temperature was 21 ± 2°. The pH values are the readings given on a pH-meter set calibrated with a commercial buffer solution of nominal pH-value as near as possible to that of the sample solution (buffers of pH = 1, 2, 3, 4, 5 or 6 were used).

RESULTS AND DISCUSSION

Figure 1 shows the results of the extraction of the various metals at different pH-values. They confirm the earlier observations on the extraction of lead and cobalt. The poor extraction of cadmium found by Kinrade and Van Loon[3] in the pH range 4–6 was not found here. The wide extraction range for nickel found here has not previously been reported. An "optimum" value for the extraction of any of these metal ions does not exist, in the sense that there is not a particular pH-value that gives better extraction than other values slightly different from it. Thus, there is no need for precise pH control anywhere in the range 1–6.

Table 1 shows half-life values ($t_{1/2}$) for PDC in water, MIBK and some two-phase systems. The $t_{1/2}$ values found here for PDC in water are somewhat lower than those reported by Aspila *et al.*,[6] but are in fair agreement with those of Everson and Parker.[2] The rate of decomposition of PDC extracted into MIBK is low. However, the rate of decomposition of PDC in the two-phase system water/MIBK is very much greater than in either single-phase system. The $t_{1/2}$ value was found to depend on the contact area between water and MIBK. In keeping with this, shaking of the mixture greatly promotes the decomposition. As $t_{1/2}$ is not affected very much if the water contains 10% of acetone (v/v), the MIBK dissolved in the water (about 2%) should not affect the rate of decomposition. This rapid decomposition is also observed when instead of MIBK the corresponding alcohol, 4-methylpentan-2-ol, is used. Chloroform does not increase the rate of decomposition. The $t_{1/2}$ for the water/MIBK system did not change when the experiment was performed in the dark and with oxygen absent. It is suggested that the decomposition of PDC proceeds rapidly at the phase boundary between water and MIBK or similar organic compounds with polar groups.

Tables 2–4 show that the time stability of the metal ion PDC complexes in MIBK depends on the metal ion and on the treatment of the extract.

In the light of the results discussed here, the time instability of the extracted metal complexes may be described as follows. Kinetically labile complexes will

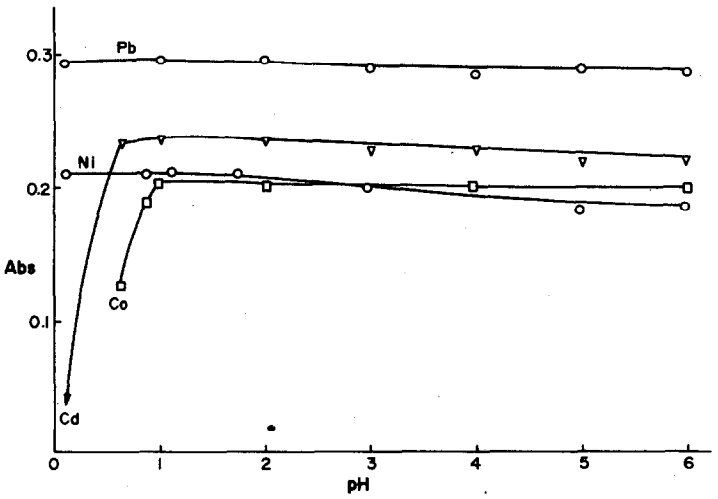

Fig. 1. Effect of pH on the amount (expressed in terms of absorbance) of Co, Ni, Cd and Pb extracted with APDC/MIBK.

Table 1. Half-life for PDC at 21 ± 2°

Conditions	$t_{1/2}$
In 0.8*M* HCl	18 ± 5 min
In acetate buffer, pH = 5.0	25 ± 3 hr
In acetate buffer, pH = 4.3	6.0 ± 0.5 hr
In acetate buffer, pH = 4.5, 10% v/v acetone added	6.0 ± 0.5 hr
In MIBK, extracted from 0.8*M* HCl	18 ± 3 hr
In MIBK, extracted from acetate buffer, pH = 5.0	22 ± 3 hr
Two phases:	
MIBK/0.8*M* HCl, intermittent shaking*	4 ± 1 min
MIBK/acetate buffer, pH = 5.0, continuous shaking	2.5 ± 0.5 min
MIBK/acetate buffer, pH = 5.0, intermittent shaking	12 ± 3 min
MIBK/acetate buffer, pH = 4.3, in dark, stirred by bubbling nitrogen gas	2.5 ± 1 min
$CHCl_3$/acetate buffer, pH = 4.3, intermittent shaking	6.2 ± 0.5 hr
MIAA†/acetate buffer, pH = 4.3, intermittent shaking	5 ± 1 min

* The flask was inverted once every minute.
† 4-Methylpentan-2-ol.

Table 2. Time stability of Cd/PDC extracts in MIBK at various pH-values of the aqueous phase

pH		Absorbance × 1000 1 hr	4 hr	7 hr	24 hr	30 hr	48 hr	80 hr
1.0	Unstirred	160	157	157	145	130	22	0
	Stirred	160	155	157	4	0		
2.0	Unstirred	158	157	158	146	149	145	50
	Stirred	159	157	159	142	68	0	
3.0	Unstirred	156	157	156	146	145	144	147
	Stirred	156	158	158	152	152	126	68

decompose when the concentration of free ligand has decreased below the level necessary for the formation of the extractable (*i.e.*, neutral) complex (the decomposition products of the ligand may also react with the metal ions to form precipitates). If the MIBK extract is separated from the aqueous phase, the rate of decomposition of the ligand will be low and the extracts will be stable for a long time (Table 4). When the MIBK phase is not separated from the aqueous phase, the decomposition will be faster and will depend on the treatment of the extracts. The decomposition is accelerated when there is a large contact

Table 3. Time stability of Co, Ni, Cd, Pb/PDC solutions in MIBK; extraction at pH = 1

		Absorbance × 1000 45 min	3 hr	7 hr	24 hr	48 hr	105 hr
MIBK-phase over pure water	Co	104	116	113	113	113	114
	Ni	99	100	102	107	—	112
	Cd	111	110	108	113	111	112
	Pb	101	101	107	111	—	123
MIBK-phase over aqueous phase at pH = 1: slow stirring	Co	103	116	114	112	116	115
	Ni	96	98	104	98	—	81
	Cd	112	109	110	0		
	Pb	102	102	111	40	—	0
MIBK-phase over aqueous phase with pH = 1: rapid stirring	Co	103	117	120	120	118	116
	Ni	95	100	103	98	—	68
	Cd	110	107	0			
	Pb	104	103	112	0		

Table 4. Time stability of Ni, Cd, Pb/PDC solutions in MIBK; extraction at pH = 1.0; MIBK-solution separated from the aqueous phase

Element	Absorbance × 1000			
	3 hr	22 days	30 days	70 days
Ni	258	266	229	209
Cd	197	198	195	191
Pb	188	190	194	184

area between the two phases (produced by the geometry of the system or by shaking), and when the acidity of the aqueous phase is increased.

The rate of decomposition decreases in the order Cd > Pb > Ni > Co. The cobalt complex is oxidized by air to $Co(PDC)_3$. One report[16] claims that this complex is not inert, which is at variance with other reports on related systems.[5,17] Experiments on the exchange between Ni^{2+} and bis(di-n-propyldithiocarbamate)nickel(II) in acetone have shown that the rate of exchange is very low.[18] We are not aware of any data for lead and cadmium, but their PDC complexes are probably labile. The order of decomposition found here is the same as that found by Usatenko and Tulyupa for the corresponding DDC complexes.[19] Our results may explain why Tweeten and Knoeck had difficulties with DDC/isoamyl alcohol extractions, as they used very long times for the separation of the phases.[7] The decrease in extraction of cadmium with increase in shaking time[13] also conforms with the findings discussed here. It should, however, be emphasized that factors other than ligand decompositions, such as adsorption,[10] are important for the stability of the extracts.

In this laboratory the following practice has been found satisfactory. Extractions are carried out in standard flasks. After shaking, the MIBK phase is raised into the neck of the flask by addition of water. All of the MIBK should be in the neck of the flask. The added water will then form a "buffer" between the organic layer and the extracted aqueous sample, where the pH is around 1. Care is taken to avoid shaking or stirring the flasks. Even the cadmium complex will then be stable for at least 2 days.

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HYDROXIDE COMPLEXES OF LANTHANIDES—II†

SAMARIUM(III) IN PERCHLORATE MEDIUM

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Summary—From the precipitation borderline in the pM′–pH diagram, determined experimentally under CO_2-free conditions, the stability constants of the mononuclear and polynuclear species of samarium hydroxide have been established. The values found are $\log {}^*\beta_1 = -7.5$, $\log {}^*\beta_2 = -15.0$, $\log {}^*\beta_3 = -22.7$, $\log {}^*\beta_{4,3} = -19.5$ and $\log {}^*K_{s0} = 17.5$. They refer to fresh precipitates, prepared at room temperature in sodium perchlorate medium with an ionic strength of 1.

In a previous paper[1] a method was described for the determination of the hydrolysis constants of metals from the precipitation borderline in a pM′–pH diagram. This method was applied to cerium(III) and yielded such promising results that further experiments were undertaken for the other lanthanides. In this paper the hydrolysis of samarium(III) will be discussed. Not all the hydrolysis constants of Sm(III) are known, and those published show a remarkable diversity. Moeller[2] reported different values for $\log {}^*\beta_1$; depending on the concentration of the samarium sulphate solution used (0.05–0.001M), he found $\log {}^*\beta_1$ values ranging from -10.7 to -9.1. Baes and Mesmer[3] applied the empirical relation $\log {}^*K_{LnL} = \log {}^*K_{LaL} + b$, which was proposed by Kumok and Serebrennikov,[4] and found $\log {}^*\beta_1 = -7.9$ ($I = 0$), -8.2 ($I = 0.05$) and -9.6 ($I = 3$). Furthermore they reported $\log {}^*\beta_{22} = -13.8$ ($I = 3$) and $\log {}^*K_{s0} = 16.5$ ($I = 0$); the last constant was deduced from considerations about lattice parameters. Guillamont *et al.*[5] determined $\log {}^*\beta_1$ by means of solvent extraction and radiochemical measurements. For lithium perchlorate medium ($\mu = 0.1$) and pH 2.5–5 they found $\log {}^*\beta_1 = -4.4$. Kovalenko *et al.*[6] investigated the composition of samarium hydroxide complexes by an oscillopolarographic method. For solutions containing samarium chloride in concentrations between 2×10^{-4} and $6 \times 10^{-4} M$ they concluded that $Sm(OH)Cl_2$ was precipitated in the pH range 6.30–6.55, and $Sm(OH)_2Cl$ in the pH range 6.65–6.80. In their opinion, solid $Sm(OH)_3$ is formed only at pH ≥ 6.8; $\log {}^*K_{s0} = 16.8$ (20°, $I = 0$). From pH-titrations Meloche and Vrántý[7] calculated $\log {}^*K_{s0} = 21.3$ (20°, $I = 0.1$) from the points in the titration curves corresponding to precipitation of half of the initial samarium perchlorate. Akselrud *et al.*[8] reported the composition $Sm(OH)_2Cl$ for freshly prepared precipitate. After aging for a month it was converted into $Sm(OH)_3$; for this aged precipitate and the experimental conditions 25°, $C_{Sm} = 10^{-4}$–$10^{-1} M$ and pH 6–7, a value of $\log {}^*K_{s0} = 16.4$ was calculated.

The diversity of these results is apparently due to the neglect of the presence of polynuclear hydroxide complexes and to the difference in the experimental conditions used. The ionic strength, the aging of the precipitate, the influence of anions which do not behave indifferently when present in higher concentrations, and the method of precipitate formation undoubtedly play an important role.

In our investigations we found that the most reproducible results were obtained with "fresh precipitates" formed under nitrogen, in a glove-box, analogously to the case of cerium(III).[1] The need to standardize the precipitation procedure is related to the fact that the release of even trace amounts of hydrogen ions in an unbuffered system near pH 7 leads to a large decrease in pH. The gradual release of hydrogen ions occurs because of absorption of CO_2 from the air, delayed precipitation, and delayed formation of soluble (polynuclear) hydroxide complexes. By strict standardization of the precipitation procedure with respect to time and by exclusion of CO_2, values for ${}^*\beta_1$ and ${}^*K_{s0}$ could be established that were consistent with those found by other investigators. Moreover, values for ${}^*\beta_2$, ${}^*\beta_3$ and ${}^*\beta_{4,3}$, absent in existing literature, have been deduced.

THEORY

In previous publications[1,9,10] it has been shown that the borderline of precipitation in the pM′–pH

† Part I: *Talanta*, 1978, **25**, 147.

diagram can be divided into straight-line segments for which the following general formula holds

$$pM'_{max} = (np-q)pH - (p \log {}^*K_{s0} + \log {}^*\beta_{q,p} + \log p) \quad (1)$$

in which ${}^*\beta_{q,p}$ is the overall stability constant of the complex $M_p(OH)_q$, ${}^*K_{s0}$ is the solubility product† and n the charge on the metal ion.

When the precipitation region in the pM'–pH diagram has been established experimentally, the straight-line segments, each with its distinct slope $(np-q)$ can be shifted so that the envelope curve fits the experimental points. From the final position of the lines the stability constants and probable composition of the hydroxide complexes can be deduced.[1]

The following theoretical remarks can be made about the influence of dissolved CO_2 on pH. The equilibrium molar concentrations of the different species derived from CO_2 in air-saturated water[10] are

$$[H_2CO_3] = 10^{-5.0} \quad (2)$$

$$[HCO_3^-] = 10^{-11.35}/[H^+] \quad (3)$$

$$[CO_3^{2-}] = 10^{-21.7}/[H^+]^2 \quad (4)$$

If the normal atmospheric CO_2 pressure ($10^{-3.52}$ atm) is decreased by a factor f through flushing of the glove-box with nitrogen, the concentrations are all decreased by this factor f.

In the pH-range of interest (pH 6–8) the concentration of CO_3^{2-} is negligible relative to $[HCO_3^-]$ and $[H_2CO_3]$. From charge balance it follows that

$$[H^+] = [OH^-] + [HCO_3^-] \quad (5)$$

Multiplication of equation (5) by $[H^+]$ and substitution of equation (3) and $K_w = 10^{-14}$ leads to

$$pH = -\tfrac{1}{2}\log\left(10^{-14} + \frac{10^{-11.35}}{f}\right). \quad (6)$$

From this equation it follows that the deviation from pH 7 (for pure water) caused by dissolved CO_2 becomes negligible for $f > 10^3$. Although strictly holding only for pure water, this inequality still informs us about the extent to which dissolved CO_2 (air) has to be removed from a solution by nitrogen in order to make its contribution to the pH-shift negligible.

Another way in which CO_2 can contribute to a pH-change is by its reaction with the ions Sm^{3+}, $SmOH^{2+}$ and $Sm(OH)_2^+$ to form an insoluble carbonate:

$$2Sm(OH)_i^{(3-i)} + 3H_2O + 3CO_2 \rightarrow \{Sm_2(CO_3)_3\}_{solid} + (6-2i)H^+ + 2iH_2O \quad (7)$$

Hydrogen ions can also be released by an analogous reaction leading to the formation of a basic carbonate. When the CO_2 initially present under air-saturated conditions has been removed by precipitation, absorption of CO_2 from the air will start and cause a slow continuation of reaction (7) (or its analogue). The pH will change gradually if no precautions are taken. It was found experimentally that decrease of the CO_2 pressure by a factor of 100 was sufficient to suppress reaction (7) to such a degree that the pH was acceptably reproducible.

EXPERIMENTAL

Nearly all manipulations were performed in a 1000-litre glove-box, flushed with nitrogen. The solutions in the box were freed from CO_2 by bubbling nitrogen through them. The effectiveness of exclusion of CO_2 was checked by introducing 1 litre of helium into the box and measuring with a helium leakage detector the He concentration of the outlet stream as a function of time. Although at a flushing rate of 0.85 l./sec the factor f should have been $> 10^3$ after 2 hr, more prolonged flushing (> 3 hr) turned out to be necessary, because displacement of the air from inside apparatus and glassware is rather inefficient.

The pH-measurements were made with a glass and calomel electrode system and a Radiometer pH-meter. The calomel electrode was filled with a concentrated solution of sodium chloride to prevent clogging of the asbestos liquid-junction bridge by the precipitation of potassium perchlorate that would have occurred if potassium chloride solution had been used instead. Bates[12,13] and McBryde[14,15] have shown that a glass and calomel electrode system can be calibrated in pC_H units when used with solutions in which an indifferent electrolyte predominates at constant ionic strength. A consistent set of buffer solutions has been prepared for calibration in concentration units by making use of the dissociation constants of phosphoric acid, boric acid and water determined by Baes *et al.*[16–18] The pC_H was measured in our perchlorate medium ($I = 1$) with a precision better than 0.02. This was satisfactory in comparison with the uncertainty in the experimental results.

The samarium solutions were prepared by dissolving commercial 99.9% Sm_2O_3 in 1*M* perchloric acid by heating. The experiments were performed with $10^{-2}M$ samarium stock solutions except for the range $pSm' < 2$, in which case a 0.1*M* solution was used.

Procedure

Add carbonate-free 50% sodium hydroxide solution dropwise to 200–300 ml of samarium perchlorate solution in 1*M* perchloric acid, with vigorous stirring, until a pH of 1 is reached. Add dilute alkali carefully until pH 4 is reached and cool the solution to room temperature. Add dilute alkali until precipitation starts. Remove a 25-ml portion. Add dilute alkali in small portions to the remainder of the solution until the pH has been increased by about 0.2. Remove a second 25-ml portion. Increase the pH again by 0.2 and remove a third 25-ml portion, but finish the three steps within a span of 15 min. Separate the precipitate and solution by decantation after exactly 30 min of aging. Centrifuge the decanted solutions in order to collect residual and colloidal particles. Withdraw aliquots from the tubes, measure the pC_H with a pH-meter calibrated in concentration units and acidify slightly. Keep the solutions for determination of samarium.

Repeat the whole procedure for the next set of three solutions. Proceed until the whole pH-range has been covered. Take the acidified solutions out of the glove box and determine their samarium content by photometric titration with EDTA, with Xylenol Orange as the indicator.[1]

RESULTS AND CONCLUSIONS

The experimental results are plotted in Fig. 1. The uncertainty in the correction to be made for ionic

† According to IUPAC notation[11]

$$\left({}^*\beta_{q,p} = \frac{[M_p(OH)_q].[H]^q}{[M]^p}, \quad {}^*K_{s0} = \frac{[M^{n+}]}{[H^+]^n}\right).$$

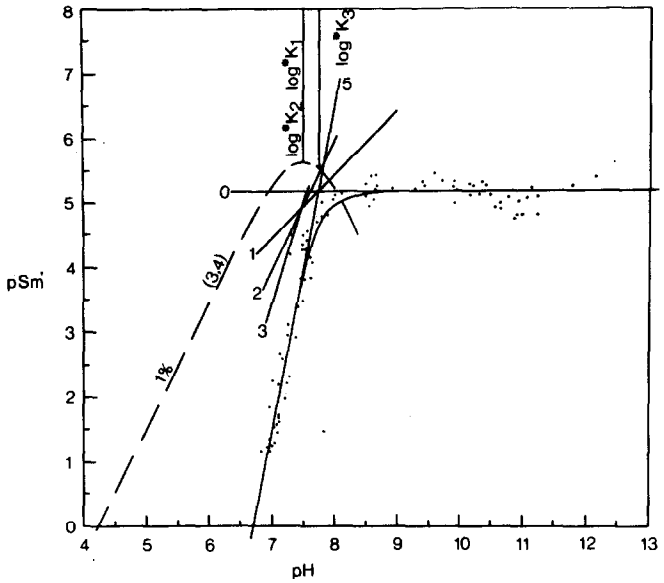

Fig. 1. The solid curve [the borderline of precipitation of $Sm(OH)_3$] has been constructed with the values given in Table 2. The dashed line is the borderline for 1% polycomplexation. The numbers 0, 1, 2, 3 and 5 near the straight lines correspond to the slopes of the straight-line segments approximating the exact envelope curve [equation (8a)–(8e)]. The dots denote the experimental results.

strengths >1 is larger than the uncertainty in the position of the experimental points. Therefore no points have been determined in the region $pSm' < 1$.

The steep part of the borderline of the precipitation region is nearly straight. Regression analysis in the range up to $pSm' = 4.6$ shows that the slope can be estimated as 5.1 ± 0.3. From this value it can be concluded that a polynuclear hydroxide complex has to be present, with a positive charge of at least 5. Although only speculative remarks can be made about the real identity of this species, $Sm_3(OH)_4^{5+}$ is assumed to be the predominant complex for the following reasons. Its charge lies close to the integral value $(3p - q) = 5$ of the slope of the straight-line segment which approximates the envelope curve in that region. Other complexes with a charge of 5+, such as $Sm_2(OH)^{5+}$ and $Sm_4(OH)_7^{5+}$, are much less likely for stereochemical and statistical reasons.[3] In principle a mixture of 2 complexes with charges greater and less than 5+ can also lead to a borderline with a mean slope of 5 and fitting the steep part well, but it is then impossible to fit the bend of the curve to the experimental points in the region pSm' 4.5–5.5, because the envelope curve, which in its steep part is then composed of two intersecting straight-line segments, has an increased curvature in that region, which makes the bend of the envelope curve pass under the experimental points.

The supposition that a polymer of charge 5+ is the only one formed in solution, leads to the following set of equations for the straight-line segments (Table 1).

Assigning equation (8a) to the steep part of the borderline (ranging up to pSm' 4.6) the best fit to the points is obtained with the equation

$$pSm' = 5\,pH - (33.5 \pm 0.1) \qquad (9)$$

which leads to the following relation between the constants:

$$3 \log {}^*K_{s0} + \log {}^*\beta_{4,3} = 33.0 \pm 0.1 \qquad (10)$$

Equation (8e) can be assigned to the horizontal part of the borderline. The best fit corresponds to

$$pSm' = 5.20 \pm 0.02 \qquad (11)$$

Table 1

Equation number	p	q	Slope $(np - q)$	Equation for the borderline segment
8a	3	4	5	$pSm' = 5pH - (3 \log {}^*K_{s0} + \log {}^*\beta_{4,3} + 0.5)$
8b	1	0	3	$pSm' = 3pH - \log {}^*K_{s0}$
8c	1	1	2	$pSm' = 2pH - (\log {}^*K_{s0} + \log {}^*\beta_1)$
8d	1	2	1	$pSm' = pH - (\log {}^*K_{s0} + \log {}^*\beta_2)$
8e	1	3	0	$pSm' = -\log {}^*K_{s3} = -(\log {}^*K_{s0} + \log {}^*\beta_3)$

$${}^*\beta_{q,p} = \frac{[Sm_p(OH)_q] \cdot [H^+]^q}{[Sm^{3+}]^p}; \quad {}^*\beta_{q,1} \equiv {}^*\beta_q \text{ and } [Sm(OH)_3]_{max} = {}^*K_{s3} = {}^*\beta_3 \cdot {}^*K_{s0}.$$

from which can be deduced

$$\log {}^*K_{s0} + \log {}^*\beta_3 = -5.20 \pm 0.02 \qquad (12)$$

If it is assumed that the straight-line segments corresponding to equations (9) and (11) are the only ones contributing to the envelope curve, the following equation holds for this curve:

$$[Sm']_{max} = 10^{-(5pH - 33.5)} + 10^{-5.2} \qquad (13)$$

With this equation an excellent fit is obtained to the experimental points in the rather sharp bend. It means that as the term in equation (13) correspond to $Sm_3(OH)_4^{5+}$ and $Sm(OH)_3$ respectively, the fresh precipitate will be in equilibrium (more or less defined) with these species only. This can be seen as follows. If, together with the precipitate, one (or more) of the species Sm^{3+}, $SmOH^{2+}$ or $Sm(OH)_2^+$ is present in measurable amount, equation (13) has to be extended with the corresponding term. The straight-line segment belonging to this term should contribute to the shape of the envelope curve. The bend of this curve is the first place where such a contribution should become manifest, as can be seen by moving the line segment (with slope 1, 2 or 3) from left to right. As without their contribution the fit of the curve to the experimental points is already excellent, it can be concluded first that there is no contribution of one of the lines corresponding to equations (8b), (8c) or (8d), and secondly that there is a limiting position for the line segments. As the straight-line segments intersect each other at $pH_i = p^*K_i$ the limiting position implies that these constants cannot exceed certain values. In Fig. 1 the envelope curve corresponds to equation (13). The straight-line approximations to this curve [equations (9) and (11)] intersect at pH = 7.74. Different plots have been made with p^*K_i values approaching 7.74. In this way it has been found that the limiting position of the other straight-line segments corresponds to $p^*K_1 = 7.5$, $p^*K_2 = 7.5$ and $p^*K_3 = 7.7$.

Consider now the 1% polycomplex borderline as a measure for the extent of polycomplexation.[1,9,10] The steep left-hand side of this borderline can be approximated by a straight-line segment given by

$$pM_{3,4}^{1\%} = 2pH + \tfrac{1}{2}\{\log {}^*\beta_{4,3} + 2.5\} \qquad (15)$$

Through equations (10) and (12) the value of ${}^*\beta_{4,3}$ is related to the values of the other constants. Thus the extent of the polycomplex region depends upon the p^*K_i values ($i = 1, 2, 3$). As an increase in p^*K_i leads to a decrease of this region, the polycomplex region will be minimal for the limiting set of p^*K_i values already mentioned. Figure 1 is drawn for this limiting situation. Now the question remains whether p^*K_i can adopt lower values. Here we have to rely upon information from other investigators.[2,4] As lanthanide ions are fairly large, hydrolysis does not become appreciable at normal concentrations (10^{-2}–$10^{-3}M$) until fairly high pH values are reached (> 5.5). Actually this sets another limit to the extent of the polycomplex region and hence lower limits to p^*K_i. Correlating this with Fig. 1 it will be obvious that the intervals over which the values of p^*K_i may vary are small. Therefore we assume that Fig. 1 represents a situation which does not deviate much from reality. It can be noted that at the same time we have fulfilled the general rule that the ratio of the consecutive stability constants should be ${}^*K_{i+1}/{}^*K_i \leqslant 1$. Although for an unambiguous establishment of the hydrolysis constants more information is necessary, preferably directly about the polycomplexation itself, we still conclude that the values given in Table 2 can be regarded as useful for describing the hydrolysis of samarium.

Table 2.

$\log {}^*\beta_1 = -7.5$	$\log {}^*\beta_{4,3} = -19.5$
$\log {}^*\beta_2 = -15.0$	$\log {}^*K_{s0} = +17.5$
$\log {}^*\beta_3 = -22.7$	

Baes and Mesmer[3] reported the possibility of formation of $M(OH)_4^-$ species by lanthanides. However, no data have been found in the literature for such species of Sm(III). From our experiments at high pH no conclusions could be drawn as to whether the solubility increases or not. A different experimental method is necessary to obtain significant results at pH above 12.

DISCUSSION

In our opinion it is rather speculative to discuss the errors in the different constants. It is more appropriate to assign an uncertainty of about 0.1 log unit both in pSm' and pH to the position of the calculated precipitation borderline. Comparing our values with the literature data, we noticed that polycomplexation has often been neglected,[2,4,6,7] that interaction with sulphate has not been taken into account[2] or that the adopted extraction model is obviously too simple.[5]

When corrected for differences in ionic strength, our value for $\log {}^*\beta_1$ was found to be in fair agreement with that of Kumok and Serebrennikov,[4] although they used a statistical method, based on data for ligands other than OH^-. Comparing the $\log {}^*K_{s0}$ values, also after correcting for differences in ionic strength, our value ($\log {}^*K_{s0} = 18.4$; $I = 0$) and the one determined by Meloche *et al.*[7] ($\log {}^*K_{s0} = 22.2$; $I = 0$) are significantly higher than those determined by the other authors ($\log {}^*K_{s0} = 16.4$–16.8; $I = 0$). These differences can be attributed to different aging times of the precipitates (Meloche *et al.*[7] 2 min, the other authors 4 hr–1 month, our work 30 min).

A fresh precipitate tends to have a higher solubility then an aged one.[1] It has been concluded that $Sm_3(OH)_4^{5+}$ is the species which is predominantly formed in the polycomplex region. Although this has not been established unambiguously, it is at any rate certain from the steepness of the corresponding part of the precipitation borderline that $Sm_2(OH)_2^{4+}$ is not formed to a measurable extent. So the results of

Kumok and Serebrennikov[4] found by interpolation are questionable.

Summarizing, it can be stated that with the method previously applied to Ce(III) valuable information can be obtained about the occurrence of the various samarium hydroxide species and the magnitude of their stability constants. Further experiments are in preparation for the other lanthanides.

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HANDLING OF ELECTRONIC ABSORPTION SPECTRA WITH A DESK-TOP COMPUTER—II*

CALCULATION OF STABILITY CONSTANTS FROM SPECTROPHOTOMETRIC TITRATIONS

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Summary—A fully automatic system for combined spectrophotometric and pH titrations was described in Part I. Its performance in the titration of weak acids and metal complexes is discussed, along with a computer program for numerical treatment of the data, based on Marquardt's modification of the Newton–Gauss non-linear least-squares method. The deprotonation of *p*-nitrophenol at concentrations of 4×10^{-5} and $4 \times 10^{-6} M$ was studied in order to test the sensitivity. Results identical within the reproducibility of the pH-meter were obtained: $pK^H = 7.00 \pm 0.01$ and 7.02 ± 0.01, respectively. Three complexation reactions were studied: (*1*) the interaction of SCN^- with the Co^{2+} complex of 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (TMC); five independent experiments gave pK $[CoTMC(SCN)^+ \rightleftharpoons CoTMC^{2+} + SCN^-] = 3.099 \pm 0.003$: (*2*) the deprotonation of the Cu^{2+} complex of 3,7-diazanonanediamide (DANA); five experiments gave pK $(CuDANA^{2+} \rightleftharpoons CuDANAH^+_{-1} + H^+) = 7.14 \pm 0.01$ and pK $(CuDANAH^+_{-1} \rightleftharpoons CuDANAH_{-2} + H^+) = 8.38 \pm 0.01$: (*3*) for the reaction of Cu^{2+} with 1,3,7-triazacyclodecane (L), data from different ligand:metal ratios had to be combined to obtain pK $(CuL^{2+} \rightleftharpoons Cu^{2+} + L) = 16.19 \pm 0.01$, pK $(CuL_2^{2+} \rightleftharpoons CuL^{2+} + L) = 10.30 \pm 0.01$, and pK $(Cu_2L_2(OH)_2^{2+} \rightleftharpoons 2\,CuL^{2+} + 2\,OH^-) = 14.58 \pm 0.03$. Titration curves with a total change in absorbance of as little as 0.03 units could be analysed satisfactorily, extending considerably the useful range of concentrations for spectrophotometric titrations. In combined spectrophotometric/pH titrations the accuracy of the glass electrode is normally the limiting factor. Other equilibrium constants can easily be reproduced with standard errors of less than 0.01 log unit.

Although electronic absorption spectrophotometry is of very broad potential applicability in the determination of equilibrium constants, in practice its use has been limited by the need for very precise absorbance values[1] and numerical treatment of a relatively large amount of raw data with a minimum of simplifications. Several general programs, based on different algorithms, for the calculation of equilibrium constants from spectrophotometric data can be found in the literature. A program by Kankare[2] is based on a direct search method. Feldberg *et al.*[3] have used Sillén's twist matrix method.[4] Leggett and McBryde[5] describe a program based on SCOGS[6] which has been successfully applied to many equilibrium studies. Another Newton–Gauss least-squares refinement program was developed by Lingane and Hugus.[7] Recently, a program using Marquardt's[8] extension of the Newton–Gauss algorithm has been published.[9]

In Part I,[10] we described a fully automatic system for combined spectrophotometric and pH-titrations with on-line digital data acquisition by means of an HP9820 desk-top calculator. The performance of the system was tested critically and absorbance readings with a reproducibility of 0.00012–0.00017 were obtained for chemically stable test solutions. Here we report the use of this set-up in the determination of equilibrium constants for systems of increasing degrees of complexity. The reactions studied were: the deprotonation of *p*-nitrophenol (PNP), the interaction of SCN^- with the Co^{2+} complex of 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (TMC), the stepwise deprotonation of the Cu^{2+} complex of 3,7-diazanonanediamide (DANA), and the complexation of Cu^{2+} with 1,3,7-triazacyclodecane (TACD). Computer programs were developed for the calculation of equilibrium constants and molar absorptivities by using a general non-linear least-squares analysis of the Newton–Gauss–Marquardt[8] type. The programs also allow both the original absorption data and the spectra of the individual chemical species, calculated from the final set of parameters, to be plotted. The complete numerical treatment was done on a desk top calculator, HP9821, with fully expanded memory.

EXPERIMENTAL

Materials

TMC,[11,12] DANA.2HCl,[13] and TACD.3HBr,[14,15] (by the tosylate ester method[16]) were synthesized as described in the literature. Standard solutions of $CoTMC(ClO_4)_2$ were obtained from $Co(ClO_4)_2$ and TMC after filtering off excess of Co^{2+} precipitated as $Co(OH)_2$.[17] Amine-buffer

* Part I—*Talanta*, 1979, **26**, 563.

Table 1. Experimental conditions for spectrophotometric titrations

System	Titration mixtures, M		V_o ml	Titrant, ml* $V_{t,1}(\Delta V_1)$	$V_{t,2}(\Delta V_2)$	Wavelengths, nm λ_{max}	λ_{min}	$\Delta\lambda$	No. of batches
p-nitrophenol	CH_3COOH	0.0174	2.4	0.4M NaOH		440	360	10	2
	NaH_2PO_4	0.0174							
	H_3BO_3	0.0174							
	PNP: (*a*)	4×10^{-5}		0.15 (0.01)	0.14 (0.01)				
	(*b*)	4×10^{-6}							
	KCl	0×482							
$CoTMC^{2+}/SCN^-$	morpholine	0.1	2.5	$9.4 \times 10^{-3}M$ NaSCN		340	300	10	5
	$HClO_4$	0.05							
	$CoTMC^{2+}$	2×10^{-4}		0.30 (0.02)	— —				
	$NaClO_4$	0.45							
Cu^{2+}/DANA	DANA.2HCl	0.01	2.0	0.2M NaOH		700	640	10	5
	$CuSO_4$	0.009							
	KCl	0.44		0.24 (0.01)	— —				
	$pH_{initial}$	4–5							
Cu^{2+}/TACD	TACD.3HBr	0.002	2.5	0.05M NaOH		780	540	20	2
	$CuSO_4$ (*a*)	0.0018							
	(*b*)	0.0009		0.30 (0.03)	0.11 (0.01)				
	KNO_3	0.5							

* $V_{t,i}$: total amount of titrant added with increments ΔV_i.

bases were distilled before use. Other analytical grade reagents were used without further purification. All experiments were done at 298 K in doubly distilled water. The ionic strength was adjusted to 0.5. The experimental conditions for the spectrophotometric titrations are summarized in Table 1.

Computer programs

The computer program for on-line data acquisition was described in Part I.[10] A general program has been developed for (*i*) plotting the absorbance data after correction for the baseline, (*ii*) non-linear least-squares calculation of equilibrium constants and molar absorptivities from data at specified wavelengths and plotting of the experimental and calculated titration curves, and (*iii*) calculation and plotting of the absorption spectra of the individual species from the final set of equilibrium constants (weighted mean of results obtained at the different wavelengths). Although the HP9821 desk-top calculator had a fully expanded memory of 1447 registers, space limitations were rather severe and it was necessary to take great care to write the program as concisely as possible. Six hundred registers (roughly 2.5 kbyte) were left for the numerical data and the subroutine describing the equilibrium system. In order to increase the amount of data which could be treated, the program was also divided into three independent parts for tasks (*i*)–(*iii*). Because of extensive use of the same subroutines in all three parts, the effect of splitting is not dramatic, but roughly 100 registers of memory can be saved.

Below we describe these separate programs, rather than the combined one, in some detail.

(*i*) *Plotting of experimental data.* This program is simple in concept. First the data accumulated by the on-line titration system[10] are read in from tape, then the baseline is subtracted from the data and the extremes of the absorbance values are found. The program calls a general plotting subroutine which automatically sets the proper limits and labels the axes. Finally the individual corrected absorbance values are plotted and connected by curves obtained from fourth-order polynominals. Up to 30 curves are identified by the successive use of ten different symbols and solid, broken or dotted lines, respectively.

(*ii*) *Calculation of equilibrium constants and molar absorptivities at specified wavelengths.* After the subroutine describing the chemical system and the data has been read in, the baseline correction is applied and the absorbance values are ordered according to wavelength and rewritten onto the tape in individual data files. The values for equilibrium constants known from previous experiments and estimates for those to be determined are then read in, followed by the number of absorbing species. Next, the program asks for the wavelength to be used in the calculation. Subroutines are called to calculate the concentrations of all absorbing species at each point of the titration curve,* the absorptivities of all species, the residuals in absorbance (difference between experimental and calculated absorbance), and the error-square sum. The latter is printed and compared with the previous one. If the error-square sum remains constant within one part per thousand and some other termination criteria are met (*cf.* Fig. 1), the final values of the equilibrium constants and absorptivities are printed, along with their standard errors. If required, the calculated and experimental absorbances may be printed and/or the titration curve may be plotted. The program then asks for the next wavelength to be used. This part can easily be made fully automatic if the calculation is to be done successively at all wavelengths.

If the termination criteria are not met after the calculation of an error-square sum, the Newton–Gauss–Marquardt[8] non-linear regression analysis routine is called for calculation of better estimates of the equilibrium constants. In cases where sufficiently good estimates for the unknown equilibrium constants are available, the normal Newton–Gauss procedure is used alone in our program, since this is then the most rapid algorithm. A Marquardt correction is applied to the diagonal elements of the curvature matrix (*cf. e.g.*, Bevington[19]) only if divergence occurs. A flow diagram of this part of the program is given in Fig. 1.

(*iii*) *Calculation and plot of absorption spectra of the individual species.* This program is quite similar to (*ii*) except that the non-linear iteration procedure is missing. Calculation of the absorptivities of all species on the basis of the final set of equilibrium constants proceeds automatically from the maximum to the minimum wavelength. The absorption spectra for the individual species are plotted. The final set of absorptivities is stored on tape.

* These subroutines are essentially as described earlier.[18]

RESULTS

As described, equilibrium constants K_λ and their standard errors were calculated at suitable wavelengths λ for each system. Unit weights were assigned to the individual absorbance readings throughout. Weighted means, log K, were obtained from the values of log K_λ, and are compiled in Table 2 along with their standard errors $\sigma(\log K)$. In every case the weights $\sigma_\lambda = \sigma(\log K_\lambda)$ were used in the absolute (σ_a) and the relative (σ_r) form and the larger value is given in Table 2.

$$\sigma_a^2 = 1\Big/\left(\sum_{i=1}^{I} 1/\sigma_{\lambda,i}^2\right) \tag{1}$$

$$\sigma_r^2 = \frac{\sum_{i=1}^{I} (1/\sigma_{\lambda,i}^2)(\log K_{\lambda,i} - \log K)^2}{\left[(I-1).\sum_{i=1}^{I} 1/\sigma_{\lambda,i}^2\right]} \tag{2}$$

I = number of wavelengths.

As indicated in Table 2, the standard deviations in absorbance σ_A for individual titration curves were in general between 0.0002 and 0.0006, close to the intrinsic precision of the titration system.[10] Values of σ_A were between 0.0006 and 0.0018 for $4 \times 10^{-5} M$ PNP and for Cu^{2+}/DANA with higher total changes in absorbance (between 0.3 and 0.8 units), reflecting the uncertainty of the pH readings through the law of error propagation. Equilibrium constants of essentially the same quality were obtained, whether the total change in absorbance was as low as 0.03 or as high as 0.8.

The reproducibility of the titration system was studied with $CoTMC^{2+}/SCN^-$ and Cu^{2+}/DANA, for which the experiment was repeated five times and the variance between results from different batches could be estimated along with the standard errors for log K as obtained from a single experiment. The averages of log K ($\overline{\log K}$) and their standard errors $\sigma(\overline{\log K})$ are included in Table 2 for these two systems.

Individual titration curves for the deprotonation of PNP could be fitted very closely: $\sigma(\log K)$ values of 0.001 and 0.002 were obtained for 4×10^{-5} and $4 \times 10^{-6} M$ PNP, respectively. The latter result is

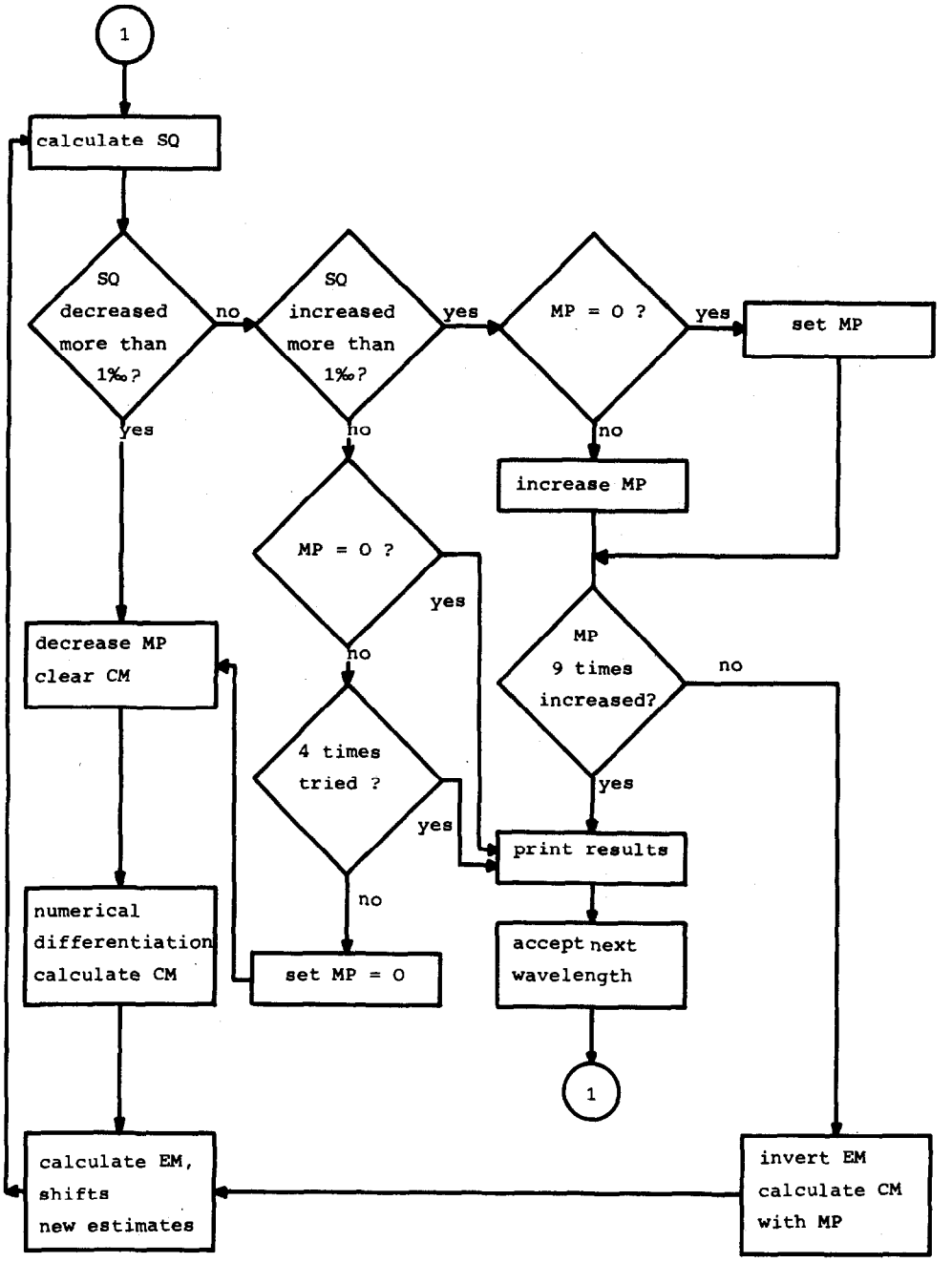

Fig. 1. Flow diagram of the non-linear regression analysis. SQ: Error-square sum, sum of squares of residuals; MP: Marquardt parameter;[8] CM: curvature matrix;[19] EM: error matrix.[19]

remarkable since, depending on the wavelength chosen, the total changes in absorbance were as low as 0.02–0.06, in the experiment with the lower concentration of PNP. Since 30 spectra were recorded per titration, changes in absorbance between two titration steps were typically around 0.001–0.002, and apparently even such small changes could be determined quite accurately.

Probably the main source of error is the glass electrode. The precision of equilibrium constants obtained from combined spectrophotometric and pH-titrations was considered to be ± 0.01 log units at best and no standard errors below this limit are listed for the final results of such experiments. Within the uncertainty expected from the use of the pH-meter the results for 4×10^{-5} and for $4 \times 10^{-6} M$ PNP are identical.

The complexation between $CoTMC^{2+}$ and SCN^- was studied between 340 and 300 nm. Total changes in absorbance were between 0.04 and 0.12 (depending on the wavelength), significantly below the optimum range of the spectrophotometer. From five independent experiments, values of 3.101 ± 0.005, 3.089 ± 0.006, 3.108 ± 0.006, 3.103 ± 0.006, and

Table 2. Results of combined spectrophotometric and potentiometric titrations

Reaction	log K* ($\sigma \times 10^3$)				$\overline{\log K} \pm \sigma$†	$n\lambda$§	np§	$\sigma_A \times 10^4$§
	([PNP] = $4 \times 10^{-5}M$)	([PNP] = $4 \times 10^{-6}M$)						
$PNPH_{-1} + H^+ \rightleftharpoons PNP$	6.999 (1)				7.01 ± 0.01	(7.149)‡	9	30	7–18
$CoTMC^{2+} + SCN^- \rightleftharpoons CoTMC(SCN)^+$	7.016 (2)								
$CuDANAH^+_1 = H^+ \rightleftharpoons CuDANA^{2+}$	3.101 (5)	3.089 (6)	3.108 (6)	3.103 (6)	3.094 (6)	3.099 (3)	(3.07 ± 0.04)‡	5	16	2–6
$CuDANAH_{-2} + H^+ \rightleftharpoons CuDANAH^-_1$	7.161 (9)	7.164 (7)	7.137 (7)	7.142 (4)	7.133 (8)	7.14 ± 0.01	(7.14 ± 0.02)‡	7	26	4–9
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$††	8.375 (6)	8.382 (8)	8.402 (8)	8.372 (7)	8.378 (3)	8.38 ± 0.01	(8.38 ± 0.01)‡	7	26	4–9
$CuL^{2+} + L \rightleftharpoons CuL^{2+}_2$††	16.194 (7)				15.48¶	16.19 ± 0.01	(16.14 ± 0.09)‡	9	49	2–5
$2CuL^{2+} + 2OH^- \rightleftharpoons Cu_2L_2(OH)^{2+}_2$††	10.303 (10)					10.30 ± 0.01	(10.26 ± 0.04)‡	9	49	2–5
	14.582 (30)					14.58 ± 0.03	(14.52 ± 0.09)	9	49	2–5

* Weighted means from results obtained at $n\lambda$ different wavelengths. Mixed constants, with $[H^+] = 10^{-pH}$ and $K_w = [H^+][OH^-] = 1.38 \times 10^{-14}$ are given throughout.
† Because of an estimated uncertainty of 0.01 in the pH-readings a lower limit of 0.01 was set for $\sigma(\overline{\log K})$ in combined spectrophotometric and pH-titrations.
‡ Values from the literature: PNP,[20] extrapolated to zero ionic strength; $CoTMC^{2+}/SCN^-$;[21] Cu^{2+}/DANA;[13] Cu^{2+}/TACD.[15] Ligand deprotonation constants taken from the literature.[13,15]
§ $n\lambda$: number of wavelengths; np: number of points per wavelength; σ_A: range of standard deviations in absorbance.
†† L = TACD.
¶ From Zompa,[22] ionic strength = 0.1 (KNO_3).

3.094 ± 0.006 were obtained for log K ($CoTMC^{2+} + SCN^- \rightleftharpoons CoTMC(SCN)^+$). No significant differences between the experiments were found: $\overline{\log K} = 3.099 \pm 0.003$ with almost identical values for σ_a and σ_r. Thus the overall uncertainty for such complexation reactions, in which no measurement of the pH is involved, is well below 0.01 log unit.

The deprotonation of $CuDANA^{2+}$ to $CuDANAH^+_1$ and to $CuDANAH_{-2}$ was studied at 10-nm intervals between 700 and 640 nm. Formation of $CuDANA^{2+}$ is essentially complete at pH 3 and deprotonation occurs in strongly overlapping equilibria.[13] As shown in Fig. 2, hardly any indication of the presence of a two-step equilibrium is obtained from visual inspection of a titration curve. Although this makes initial estimates of the equilibrium constants somewhat arbitrary, no difficulties were encountered in the refinement process. In fact, the final values were always obtained after two refinement cycles, once the parameters had been calculated at the first wavelength. The time needed for the automatic calculation of one complete experiment for all seven wavelengths is 55 min on the HP9821.

The iteration algorithm is rather insensitive to the quality of the initial estimates for the parameters. With good starting values (within 0.1 log unit), the final results are obtained after three refinements; if both parameters are wrong by one or two orders of magnitude, five and six cycles are needed, respectively. No tendency to divergence was observed even with completely erratic initial guesses.

Standard errors of the equilibrium constants were between 0.003 and 0.009 log unit for results from different wavelengths but a single batch. For reasons discussed above, $\sigma(\overline{\log K})$ was not allowed to be below 0.01 log unit in the final results.

TACD (L) and Cu^{2+} give the complexes CuL^{2+}, CuL^{2+}_2, and $Cu_2L_2(OH)^{2+}_2$ according to results from potentiometric titrations.[15] Since CuL^{2+}_2 and $Cu_2L_2(OH)^{2+}_2$ are formed in essentially the same pH region, data from a single titration curve did not yield reliable values for the corresponding equilibrium constants. Data from two different experiments with different metal:ligand ratios had to be combined. A modification of the standard program was developed which allowed the simultaneous treatment of more than one titration curve. Also, because of the presence of 1:2 and 2:2 complexes, a more complicated subroutine using the Newton–Raphson method for iterative calculation of the concentrations of the complex species had to be applied. This longer subroutine, together with the increased number of data points, completely filled the available memory and the treatment of the data from a single wavelength needed roughly 100 min. Nevertheless, the results agree well with those obtained from purely potentiometric titrations. Log K values were calculated from data obtained between 600 and 780 nm, at 20 nm intervals. While log K ($Cu^{2+} + L \rightleftharpoons CuL^{2+}$) could be determined accurately at all wavelengths, the quality of the

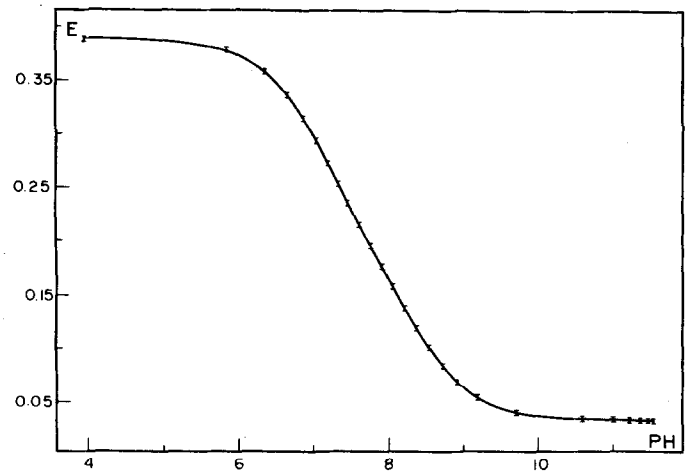

Fig. 2. Titration of $CuDANA^{2+}$ with NaOH. Conditions given in Table 1. λ = 700 nm, error bars = 5σ (absorbance) = 0.002.

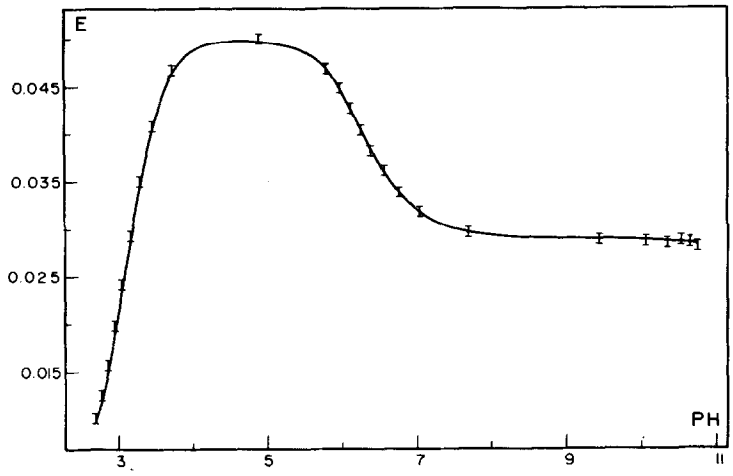

Fig. 3. Titration of Cu^{2+}/TACD with NaOH. TACD = 0.002M, $[Cu^{2+}]$ = 0.0009M, λ = 640 nm, error bars = $2\sigma_A$ = 0.001.

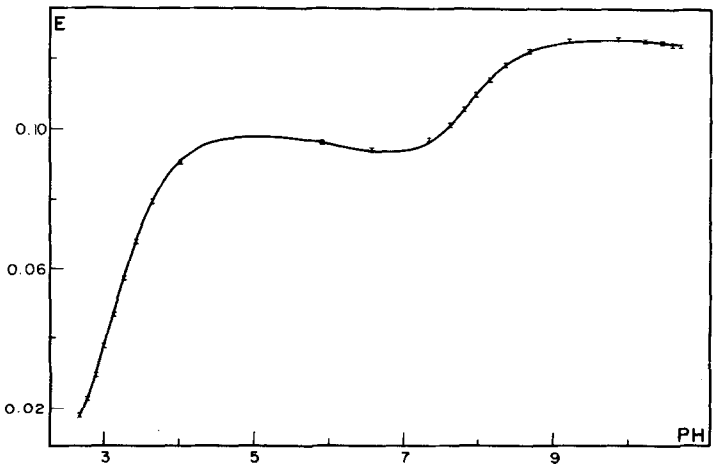

Fig. 4. Titration of Cu^{2+}/TACD with NaOH. TACD = 0.002M, $[Cu^{2+}]$ = 0.0018M, λ = 640 nm, $I = 2\sigma_A$ = 0.001.

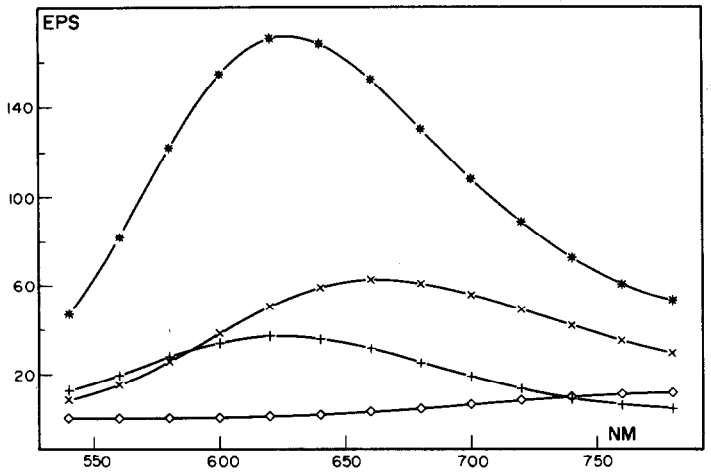

Fig. 5. Absorption spectra for complexes in the system Cu^{2+}/TACD. Molar absorptivities: ◇ Cu_{aq}^{2+}, × CuL^{2+}, + CuL_2^{2+}, *$Cu_2L_2(OH)_2^{2+}$.

results for the other equilibrium constants was strongly wavelength-dependent, since either CuL_2^{2+} or $Cu_2L_2(OH)_2^{2+}$ had absorptivities very close to those of CuL^{2+} at several λ. Titration curves for 640 nm, and Cu^{2+}:ligand ratios of 0.45:1 and 0.9:1 are given in Figs. 3 and 4, respectively.

Although the total changes in absorbance were only 0.035 and 0.1, agreement between experimental and calculated absorbances was quite satisfactory since the standard deviation in absorbance was only 0.0005 or less at all wavelengths. Finally, spectra of the individual species, as calculated from the "best" equilibrium constants, are shown in Fig. 5. Standard errors in molar absorptivity were close to 0.1 $l.mole^{-1}.cm^{-1}$ for CuL^{2+}, 0.2 $l.mole^{-1}.cm^{-1}$ for CuL_2^{2+} and 0.25 $l.mole^{-1}.cm^{-1}$ for $Cu_2L_2(OH)_2^{2+}$ at all wavelengths.

DISCUSSION

The fully automatic system for combined spectrophotometric and potentiometric titrations described previously[10] has a stability and precision such that even small total changes in absorbance of around 0.03–0.05 can be analysed without significant loss in accuracy or reproducibility. A general non-linear least-squares program* was developed for numerical treatment of the data with an HP 9821 desk-top calculator with 1447 registers of memory. For the three complexation systems studied, earlier values from this laboratory were available for comparison, mainly from potentiometric titrations.[13,15,21] As can be seen from Table 2, the new results agreed with the previous ones within their standard errors. In addition, a significant reduction in the standard errors was obtained with the new set-up.

No difficulties with convergence[1,23] were encountered in the numerical treatment of the data. For the systems PNP, $CoTMC^{2+}/SCN^-$, and Cu^{2+}/TACD this might be expected since there are no strongly overlapping equilibria. For Cu^{2+}/DANA, the precision of the initial absorbance readings might be decisive.[1] In addition, a highly effective and reliable search procedure is essential if convergence is not to depend on very good initial estimates of the parameters. The time required for lengthy graphical pretreatment of the raw data is, in our opinion, better used for carefully testing the significance of each new parameter introduced into the model describing a chemical system, and for adding as much chemical reasoning as possible when selecting the model.[5,24]

A specific problem of spectrophotometric rather than potentiometric data is, of course, the introduction of additional unknowns in the form of the molar absorptivities. Even if data from different wavelengths are treated successively rather than simultaneously, the number of unknowns is at least doubled relative to that of the same system studied potentiometrically. Three different possible ways of dealing with this problem are described in the literature. (*i*) Absorptivities and equilibrium constants are treated as two different sets of parameters. The computer alternatively calculates the best absorptivities for a given set of equilibrium constants, which is a linear problem and can be solved by simple matrix manipulation, then uses this result to obtain new estimates for the equilibrium constants, and so on, back and forth.[1,23] This method, while avoiding the manipulation of too large matrices, was found to be extremely slow in convergence for overlapping equilibria, probably because of the strong correlation between absorptivities and equilibrium constants in such systems.[7,23] (*ii*) Absorptivities and equilibrium constants are considered to be more or less equivalent parameters and are refined simultaneously.[7] This method needs estimates of both the absorptivities ϵ_j [$j = 1$ to J (number of absorbing species)] and k_i [$i = 1$ to I (number of equilibrium constants)] and the handling of matrices with dimensions $(J + I) \times (J + I)$. We found that convergence

* Listings of the program are available from the authors on request.

was relatively rapid and unproblematic when starting from reasonable estimates. (*iii*) The total number of parameters can effectively be reduced to I, the number of equilibrium constants to be refined,[25] by treating the absorbance and thence the error-square sum not as a function of the ϵ_j values and the k_i values but of the k_i values and the corresponding "best" set of absorptivities $\hat{\epsilon}_j$.

The absorptivities then disappear from the refining process. A closely related algorithm was used in the computer program SQUAD,[5] which is a modification of the well-known general non-linear least-squares program SCOGS.[6] We found this method to be by far the most effective. When it is combined with our own version of the Newton–Gauss–Marquardt algorithm for refinement of the non-linear parameters, the need for good initial estimates seems to be completely abolished and the number of iterations needed seems to depend little on the quality of the estimates, as mentioned above.

The results obtained show that equilibrium constants for simple and relatively complex systems can be obtained from automatic on-line spectrophotometric titrations and non-linear least-squares treatment of the data with a desk-top calculator. The speed of such calculators is, of course, not comparable with that of big computers, but we think that this is offset by the fact that on-line access to big computers is not always available. Slow automatic refinements can easily be done overnight or whenever the calculator is idle. The only problem with our particular calculator is the limited amount of memory (roughly 6 kbyte for programs and data combined), although this did not in fact preclude any of the planned calculations. However, combination of data from many wavelengths is not possible, unless a large amount of reading and writing data from and to tape is done, which would be very time-consuming. With the recent introduction of a new series of inexpensive desk computers with up to 48 kbyte of memory these limitations can be easily overcome and we are confident that the use of such systems will greatly further on-line data acquisition and numerical treatment of spectrophotometric and related data.

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DETERMINATION OF BISMUTH IN ORES, CONCENTRATES AND NON-FERROUS ALLOYS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY AFTER SEPARATION BY DIETHYLDITHIOCARBAMATE EXTRACTION OR IRON COLLECTION

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Summary—Two simple, reliable and moderately rapid atomic-absorption methods for determining trace and minor amounts of bismuth in copper, nickel, molybdenum, lead and zinc concentrates and ores, and in non-ferrous alloys, are described. These methods involve the separation of bismuth from matrix elements either by chloroform extraction of its diethyldithiocarbamate (DDTC) complex, at pH 11.5–12.0, from a sodium hydroxide medium containing citric acid, tartaric acid, EDTA and potassium cyanide as complexing agents, or by co-precipitation with hydrous ferric oxide from an ammoniacal medium. Bismuth is ultimately determined, at 223.1 nm, after evaporation of the extract to dryness in the presence of nitric and perchloric acids and dissolution of the salts in 20% v/v hydrochloric acid, or by dissolution of the hydrous oxide precipitate with the same acid solution, respectively. Results obtained by both methods are compared with those obtained spectrophotometrically by the iodide method after the separation of bismuth by DDTC and xanthate extractions.

A current facet of the Canadian Certified Reference Materials Project, sponsored by CANMET, is the certification of zinc, lead and copper sulphide concentrates, CZN-1, CPB-1 and CCU-1, for a number of minor and trace constituents as well as the principal metals. Recently, as part of this project, a spectrophotometric method was developed for determining bismuth, at the μg/g-level, in diverse sulphide ores and concentrates.[1] This method involves the preliminary separation of bismuth by chloroform extraction of its diethyldithiocarbamate (DDTC) complex from a strongly alkaline sodium hydroxide medium containing citric acid, tartaric acid, EDTA and potassium cyanide as complexing agents. This is followed by extraction of bismuth as the xanthate and subsequent determination as the iodide. In this work, it was suggested that moderate amounts of bismuth could probably also be readily determined by atomic-absorption spectrophotometry after separation by the relatively specific DDTC extraction step. The need for a reliable atomic-absorption method for determining ≤ 200 μg/g of bismuth in sulphide concentrates was apparent from the high results obtained in the CANMET laboratories for bismuth in CZN-1. It was also evident from the wide range of values (19–120 μg/g) obtained by atomic-absorption methods by other laboratories during the interlaboratory certification programme. Most of these methods involved neither preliminary separation nor preconcentration steps, nor matrix matching in the calibration solutions. This paper describes the application of the DDTC extraction–atomic-absorption finish to ores, concentrates and non-ferrous alloys. It also describes a simpler and more rapid atomic-absorption method based on the separation of bismuth by co-precipitation with hydrous ferric oxide. Results obtained by both methods are compared with those obtained previously by the iodide method.[1]

EXPERIMENTAL

Apparatus

A Varian Techtron Model AA6 spectrophotometer equipped with a 10-cm laminar-flow, air–acetylene burner, and the conditions recommended by the manufacturer were used for the determination of bismuth.

Reagents

Standard bismuth solution, 1000 μg/ml. Dissolve 0.5000 g of pure bismuth metal in 20 ml of concentrated nitric acid, cool and dilute the solution to 500 ml with water. Prepare a 100-μg/ml solution by diluting 25 ml of this stock solution to 250 ml with water. Prepare the diluted solution fresh as required.

Citric acid–tartaric acid solution, 25% of each acid.

EDTA, disodium salt–sodium hydroxide solution, 12% of each.

Sodium hydroxide, 50% solution.

Potassium cyanide, 20% solution. Prepare fresh as required.

Sodium DDTC, 1% solution. Prepare fresh as required. required.

Iron(III) sulphate solution (1 ml ≡ 10 mg of iron). Dissolve 25 g of ferric sulphate monohydrate in hot water

containing 5 ml of concentrated sulphuric acid, cool and dilute to 500 ml with water.

Ammonia solution 10% v/v.
Hydrochloric acid, 20% v/v.
Sulphuric acid, 50% v/v.
Nitric acid 50% v/v.
Chloroform. Analytical-reagent grade.

Calibration solutions

Add 20 ml of concentrated hydrochloric acid to eight 100-ml standard flasks; then, by burette, add to the first seven flasks 0.5, 1, 2, 3, 5, 7.5 and 10 ml, respectively, of the standard 100-μg/ml bismuth solution. The contents of the last flask constitute the zero calibration solution. If bismuth is separated by co-precipitation with hydrous ferric oxide, add 10 ml of iron(III) sulphate solution to each flask. Dilute each solution to volume with water and mix (Note 1).

Separation of bismuth by extraction of its DDTC complex

Ores and concentrates. Transfer 0.2–0.5 g of powdered sample (Note 2), containing up to approximately 1 mg of bismuth, to a 60-ml zirconium crucible. Add 3 g of sodium peroxide and mix thoroughly (Note 3). Cautiously fuse the mixture over an open flame and maintain it in the molten state for ~30 sec to ensure complete decomposition. Allow the melt to cool, then transfer the crucible to a covered 400-ml Teflon beaker containing ~80 ml of water and 25 ml of 50% sulphuric acid. When the melt has dissolved, remove the crucible after washing it thoroughly with water, then cover the beaker (Note 4) and evaporate the solution to ~75 ml. Remove the cover, add 5 ml of concentrated hydrofluoric acid and evaporate the solution to fumes of sulphur trioxide to remove silica and hydrogen peroxide. Cool, wash down the sides of the beaker with water, evaporate the solution until ~10 ml of sulphuric acid remain (Note 5), then cool to room temperature.

Add ~40 ml of water and 5 or 10 g of sodium chloride (Note 6) to the resulting solution and heat gently to dissolve the sodium salts and lead sulphate. Add 20 ml of 25% citric acid–25% tartaric acid solution, mix (Note 7) and add 50 ml of 12% EDTA–12% sodium hydroxide solution. Using a pH-meter if necessary (Note 8), or a small piece of red litmus paper added to the solution, make the solution alkaline (pH 7–11) with 50% sodium hydroxide solution. Cool the solution to room temperature in a water-bath, then adjust the pH to 11.5–12.0 with 50% sodium hydroxide solution.

Transfer the resulting solution to a 250-ml separatory funnel, add 30 ml of freshly prepared 20% potassium cyanide solution and mix thoroughly. Add 5 ml of freshly prepared 1% sodium DDTC solution, mix, then add 10 ml of chloroform (Note 9), stopper and shake for 1 min. Allow several min for the layers to separate, then drain the chloroform phase into a 150-ml beaker. Extract the aqueous phase twice more, in a similar manner, with 10- and 5-ml portions of chloroform, then wash it by shaking it for ~30 sec with 5 ml of chloroform. Add 10 ml of 50% nitric acid to the combined extracts, heat in a hot water-bath to remove the chloroform, then cover the beaker and add 10 ml of concentrated perchloric acid. Evaporate the solution to fumes of perchloric acid and continue fuming for ~15 min to ensure the complete destruction of organic material. Remove the cover, wash down the sides of the beaker with water and evaporate the solution to dryness. Add sufficient concentrated hydrochloric acid for the concentration in the final solution to be approximately 20% by volume, warm gently to dissolve the salts, transfer the solution to a standard flask of appropriate size (25–100 ml), dilute to volume with water and mix.

Measure the absorbance of the resulting solution, at 223.1 nm, in an oxidizing air–acetylene flame (Note 10). Determine the bismuth content of the solution by relating the resulting value to those obtained concurrently for calibration solutions of slightly higher and lower bismuth concentrations.

Lead-, tin- and copper-base alloys. Depending on the expected bismuth content, transfer 0.2–0.5 g of sample to a 400-ml beaker, cover and add 20 ml of 50% nitric acid. When the dissolution of the sample is complete, add 20 ml of 50% sulphuric acid and heat until the evolution of oxides of nitrogen ceases. Remove the cover, wash down the sides of the beaker with water and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool to room temperature, add ~40 ml of water and, depending on the amount of lead sulphate present, 5 or 10 g of sodium chloride (Note 6). Heat to dissolve the salts, then proceed with the addition of citric acid–tartaric acid and EDTA–sodium hydroxide solutions, the pH adjustment, the extraction of bismuth DDTC and the subsequent determination of bismuth as described above.

Separation of bismuth by co-precipitation with hydrous ferric oxide

Following the decomposition of ores and mill products and copper-base alloys (Notes 11–13) as described above, and the ultimate evaporation of the solution to fumes of sulphur trioxide, cool and add ~100 ml of water. Add 5 ml of concentrated hydrochloric acid and, if necessary, sufficient iron(III) sulphate solution for at least 100 mg of iron to be present. Cover and heat to dissolve the soluble salts. Add sufficient concentrated ammonia solution to precipitate iron as the hydrous oxide, then add 5 ml in excess and boil the solution to coagulate the precipitate. Allow this to settle, then filter hot (Whatman No. 40 paper) and wash the beaker twice and the paper and precipitate three times with 10% ammonia solution. Discard the filtrate and washings and place a 100-ml standard flask under the funnel. Wash down the sides of the beaker with 40 ml of 20% hydrochloric acid and add the resulting solution to the funnel containing the paper and precipitate. Wash the beaker twice with 20% hydrochloric acid, added from a plastic wash-bottle, and add the washings to the funnel. Wash the paper three times with the acid solution. Discard the paper. Dilute the resulting solution to volume with 20% hydrochloric acid, mix and determine the bismuth content of the solution as described above, but by comparison with absorbance values obtained for calibration solutions containing approximately the same concentration of iron(III).

Notes

1. The calibration solutions should be prepared fresh every week because they are not stable on prolonged standing.

2. Larger samples should not be used unless the volume of EDTA–sodium hydroxide solution that is employed subsequently for masking purposes is increased correspondingly.

3. If the sample contains little, or no, acid-insoluble material, it can be decomposed with acids in a Teflon beaker as follows.

Add 10 ml of 20% v/v bromine–carbon tetrachloride solution, cover and add 15 ml of concentrated nitric acid. Allow the solution to stand for ~15 min, then heat gently to remove the bromine and carbon tetrachloride. Add 20 ml of 50% sulphuric acid, heat gently until the evolution of oxides of nitrogen ceases, then remove the cover and add 5 ml of concentrated hydrofluoric acid. Evaporate the solution to fumes of sulphur trioxide, then proceed as described.

4. The solution should be kept almost completely covered during the initial evaporation, to avoid loss by spray.

5. Low results will be obtained if the solution is evaporated to dryness. If this occurs, add 20 ml each of 50%

sulphuric acid and water, heat to dissolve the salts, then evaporate the solution to fumes of sulphur trioxide and proceed as described.

6. Approximately 10 g of sodium chloride should be used if more than about 250 mg of lead is present. It can be omitted if lead sulphate is absent.

7. If the subsequent DDTC extraction cannot be performed the same day, allow the solution to stand overnight at this point. Addition of the EDTA–sodium hydroxide solution is not harmful except that the EDTA will precipitate from the acidic solution during prolonged standing.

8. A pH-meter is only necessary for highly coloured copper and nickel solutions of low iron content. If an appreciable amount of iron is present, add 50% sodium hydroxide solution until the solution changes colour because of formation of the reddish-brown iron(III)–EDTA complex.

9. Carbon tetrachloride instead of chloroform is not recommended for the extraction of bismuth from solutions containing an appreciable amount of lead. Lead DDTC, which is less soluble in this solvent, precipitates in the organic phase and may interfere mechanically with the extraction of bismuth.

10. Scale expansion (~2.5–5-fold) is recommended for the determination of approximately 1 μg/ml or less of bismuth.

11. This method is not recommended for samples containing more than 50 mg of aluminium, antimony or tin or more than 200 mg of lead.

12. Samples containing more than 1 mg of bismuth can be taken if the final solution is diluted to an appropriate volume with 20% hydrochloric acid and if the calibration solutions contain approximately the same concentration of iron(III).

13. Up to 1 g of sample can be taken if the iron content does not exceed approximately 20% and if large amounts of other elements that form insoluble hydrous oxides (Note 11) are absent. Approximately 4 g of sodium peroxide should be used for the decomposition of 1 g of sample.

RESULTS

Atomic-absorption finish after separation of bismuth by extraction of its DDTC complex

It was shown previously[1] that lead is partly co-extracted into chloroform as the DDTC complex, at pH 11.5–12.0, from a sodium hydroxide medium containing citric acid, tartaric acid, EDTA and potassium cyanide as complexing agents. Tests, in which the extract was ultimately treated with nitric and perchloric acids as described in the proposed method, showed that approximately 14–17 mg of lead are co-extracted, at the 300-mg level, when the recommended amount of sodium DDTC (50 mg) is used. However, up to at least 2000 μg/ml can be present in the final solution taken for analysis without interfering in the determination of bismuth by atomic-absorption spectrophotometry under the proposed conditions. The use of less sodium DDTC to decrease the co-extraction of lead is not recommended. It reduces the rate of complex formation and may result in incomplete extraction of bismuth. Thallium(III) is completely co-extracted as the DDTC complex but up to at least 50 μg/ml will not interfere.

Atomic-absorption finish after separation of bismuth by co-precipitation with hydrous ferric oxide

Co-precipitation procedures, involving the hydrous oxides of lanthanum,[2–5] titanium[6] and zirconium,[7] followed by an atomic-absorption finish, have been used for the separation and determination of bismuth and other elements in sulphide concentrates,[4,5] various metals[2,7] and leach solutions.[6] Iron(III) has also been recommended for co-precipitation purposes,[8,9] and has been used previously by the author for the preliminary separation of arsenic[10] and tellurium[11] from matrix elements in copper, nickel, molybdenum and zinc concentrates before their extraction as xanthates and subsequent spectrophotometric determination. Consequently, it was considered that this separation step, in conjunction with an atomic-absorption finish, should also provide a rapid, simple and reliable method for determining bismuth in diverse ores and concentrates. The use of the other co-precipitants mentioned above was not considered necessary or desirable, where only bismuth is concerned, because most sulphide ores and concentrates usually contain sufficient iron to co-precipitate small amounts of bismuth completely. Furthermore, large amounts of these elements, in conjunction with a large amount of iron, not only increase the metal ion content of the final solution, but also produce a bulky precipitate that is slow to filter and dissolve.

Tests, in which bismuth was separated by co-precipitation with 100 mg of iron(III), as described previously,[10,11] followed by dissolution of the precipitate in 20% hydrochloric acid, yielded complete recovery of 20- and 1000-μg amounts of bismuth. Further tests showed that up to 50 mg (or 500 μg/ml in the final solution) of manganese(II), antimony(V), zirconium, aluminium and tin(IV), which also form insoluble hydrous oxides, will not interfere either in the co-precipitation or in the subsequent determination of bismuth by atomic-absorption spectrophotometry. Larger amounts of tin and antimony cause low results for bismuth because of the slow and incomplete dissolution of the precipitate. A larger amount of aluminium results in a solution that passes very slowly through the filter paper. It also causes slightly high results for bismuth. Up to at least 2000 μg/ml of lead and iron(III), 500 μg/ml of nickel, copper(II), sodium and zinc, 300 μg/ml of molybdenum(VI) and arsenic(V), and 50 μg/ml of indium and thallium(III) can be present in the final solution, without interfering in the determination of bismuth. More than ~2000 μg/ml of lead may result in the precipitation of lead chloride in the solution.

Applications

To test the reliability of the proposed methods, they were applied to the analyses of the CCRMP zinc, lead and copper concentrates, CZN-1, CPB-1 and CCU-1, and to two CCRMP reference ores, MP-1 and PR-1, that have been certified for bismuth. The methods, where applicable, were also applied to certified reference copper-, tin- and lead-base alloys. The results of these analyses are given in Table 1. Except as indicated in the footnotes to Table 1, 0.5-g samples were taken in these tests.

Table 1. Determination of bismuth in CCRMP reference ores and concentrates and in NBS and BCS non-ferrous alloys

Sample	Nominal composition, %	Certified value and range, % Bi	Bi found, %		
			Iodide method	Atomic-absorption spectrophotometry DDTC extraction method	Atomic-absorption spectrophotometry Iron collection method
MP-1 Zinc–tin–copper–lead ore	15.9 Zn, 2.4 Sn, 2.1 Cu, 1.9 Pb, 5.7 Fe, 0.8 As, 19.4 Si, 3.6 Al, 3.4 Ca	0.024 (0.022–0.026)*	0.022	0.023†	0.022‡§
PR-1 Molybdenum ore	39.2 Si, 1.3 Fe, 0.6 Mo, 2.4 Al, 1.4 Ca, 2.0 K	0.111 (0.107–0.114)*	0.107	0.113†	0.109‡
CPB-1 Lead concentrate	64.6 Pb, 4.4 Zn, 8.5 Fe, 17.8 S	0.023 (0.021–0.024)*	0.022‖	0.023‡	0.021‡¶
CZN-1 Zinc concentrate	44.5 Zn, 7.4 Pb, 11.0 Fe, 30.2 S	0.0025[a]	0.0023[b]	0.0023†	0.0022‡§
CCU-1 Copper concentrate	24.7 Cu, 30.7 Fe, 3.2 Zn, 35.6 Si	—	0.0032	0.0036†	0.0037‡
NBS-C1100 Cartridge brass	67.4 Cu, 32.2 Zn	0.0010	0.0011	0.0011	0.0007
NBS-C1101 Cartridge brass B	69.5 Cu, 30.3 Zn	0.0004	0.0004	0.0003	—
NBS-C1102 Cartridge brass C	72.9 Cu, 27.1 Zn	0.0005	0.0006	0.0006	—
NBS-53d Lead-base bearing metal	9.9 Sb, 4.9 Sn	0.135 (0.12–0.143)	0.141	0.145	0.140c
NBS-54D Tin-base bearing metal	88.6 Sn, 7.1 Sb, 3.6 Cu, 0.6 Pb	0.044 (0.037–0.050)	0.048	0.050	—
NBS-127A Solder	30.0 Sn, 0.8 Sb	0.036 (0.031–0.04)	0.039	0.035	—
BCS-178 White metal "B"	84.0 Sn, 7.5 Sb, 4.1 Cu, 3.9 Pb	0.005 (0.003–0.008)[d]	0.0030	0.0038	—
BCS-183/3 Leaded gunmetal	84.5 Cu, 6.7 Sn, 3.3 Zn, 3.4 Pb, 1.5 Ni	0.008 (0.007–0.010)	0.0072	0.0072	0.0068
BCS-207/2 Gunmetal	87.3 Cu, 9.7 Sn, 1.6 Zn, 0.7 Pb	0.04 (0.039–0.048)	0.042	0.045	0.041

* 95% confidence limits of the recommended mean value.
† Sample decomposed by fusion.
‡ Sample decomposed with acids as described in Note 3.
§ 1 g sample taken.
‖ Mean of 10 values ranging from 210 to 221 μg/g.
¶ 0.28 g sample taken.
[a] Consensus mean of 130 results (excluding gross outliers) reported during the interlaboratory certification programme.
[b] Mean of 10 values ranging from 21.2 to 24.4 μg/g.
[c] 0.1 g sample taken.
[d] Certified value based on the 2 results shown in brackets.

DISCUSSION

Table 1 shows that the results obtained for the CCRMP reference ores and concentrates and for the National Bureau of Standards and British Chemical Standards non-ferrous alloys (where applicable) by the two methods, which involve completely different separation procedures, are in excellent agreement with each other, with those obtained previously by the author using the DDTC-xanthate extraction–iodide method,[1] and with the respective certified values. Unfortunately, a consensus value is not available for the CCRMP copper concentrate, CCU-1, because it was not analysed for bismuth during the interlaboratory certification programme. Furthermore, only a consensus value is available for CZN-1 because it could not be certified for bismuth. The precision of the results obtained for CZN-1 by the three methods suggests strongly that the wide range of values obtained in the interlaboratory certification programme is due to uncompensated interelement and/or matrix effects. These effects, as shown by the results obtained by one laboratory (0.0024%), can be minimized by simulating the composition of the sample in the calibration solutions. However, the inherent disadvantage in this method is that it is only applicable to samples in which the approximate content of the predominant matrix elements is known. Similarly, although matrix effects can also be eliminated, to some extent, by using the standard additions method, the results obtained by another participating laboratory (0.0092%), and work by other investigators,[12] has shown that this method is not always reliable.

In the proposed method based on the separation of bismuth by extraction of its DDTC complex, the addition of lead, before the extraction, to eliminate interference from molybdenum and zinc, as described previously,[1] is not necessary. These elements only cause low (unexplained) results for bismuth if it is subsequently stripped from the extract by shaking it with 12*M* hydrochloric acid. Earlier,[1] the author stated that the probable lower limit of this method is about 0.01%. However, this estimate was not based on the use of scale expansion for the determination of bismuth. If an expanded scale is used, the method is suitable for samples containing ~0.0005% or more of bismuth. If desired, this lower limit can be decreased to ~0.0002% if the salts ultimately obtained are dissolved in 2 ml of concentrated hydrochloric acid and the resultant solution is diluted to 10 ml. A method involving the extraction of an analogous bismuth complex, formed with ammonium pyrrolidinedithiocarbamate, into methyl isobutyl ketone, at pH ~ 10.5, from an EDTA–potassium cyanide–citrate medium, followed by the direct atomic-absorption determination of bismuth in the extract has been reported.[13] However, although it has been shown that this method yields excellent results for bismuth in non-ferrous alloys, the proposed method is more suitable for routine work because of the greater stability and ease of preparation of aqueous calibration solutions.

The method based on co-precipitation of bismuth with iron(III) is suitable for samples containing ~0.001% or more of bismuth if a 1-g sample is taken. This lower limit can also be decreased to ~0.0005% if the solution obtained after dissolution of the precipitate is concentrated by evaporation and ultimately diluted to 50 ml. This method is not recommended for samples of high aluminium, tin, antimony and/or lead contents. Both methods are also applicable to nickel and molybdenum ores and concentrates.

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EXTRACTION CHROMATOGRAPHY OF NOBLE METALS WITH USE OF MIXTURES OF HYDROCHLORIC AND NITRIC ACID AS MOBILE PHASES

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Summary—The chromatographic behaviour of the platinum metals and gold, silver and copper on paper strips treated with liquid anion-exchangers and eluted with mixtures of HNO_3 and HCl was investigated. It was found that increase of HNO_3 concentration in the acid mixture increases the R_F values more significantly than does that of HCl. The presence of HNO_3 in the development solution prevents the reduction of iridium(IV). The R_F values of the noble metals increase in the order Au(III) < Os(IV) < Ir(IV) < Pt(IV) < Pd(II) < Ru(III) < Rh(III) ~ Ir(III). Several separations of noble metals were carried out on paper strips treated with trioctylamine or quaternary alkylammonium salts, as well as the column separation of the mixture Pt–Pd–Rh. The proposed chromatographic systems seem to be especially useful for the separation of non-volatile noble metals.

The classical separation methods are not always satisfactorily selective for the platinum metals and it is often difficult to obtain the single metals in high purity from their mixtures. Therefore, it is not surprising that a search is made for rapid and more effective separation methods, for analytical and industrial purposes. The most promising separation methods for platinum metals seem to be ion–exchange chromatography and liquid–liquid extraction;[1–8] however, the problem of easy and rapid separation of platinum, palladium, iridium and rhodium has not yet been completely solved. Ion-exchange chromatography has been applied successfully for the separation of noble metals from other metals and from each other and many useful cation- and anion-exchange procedures have been described;[1,4,7,8] however, their use in analytical practice is often limited by incomplete elution (two bands are often formed for the same metal ion, owing to hydrolysis or reduction).[9–11] Further, the chloride complexes of platinum(IV) and iridium(IV) are very strongly retained on anion-exchange resins and can only be eluted with concentrated mineral acid solutions, which makes quantitative analysis of the eluate more difficult.

Extraction chromatography appears to be one of the most promising separation methods for metals,[12] but it has seldom been applied for the separation of noble metals. Pohlandt and Steele[13] separated the non-volatile noble metals on Kel-F treated with tributyl phosphate, by stepwise elution with sulphuric and hydrochloric acid; however, this interesting procedure is rather time-consuming owing to the three successive column separations required. The separation of halide complexes of platinum metals on supports treated with tertiary long-chain amine salts or quaternary alkylammonium salts is difficult owing to the very strong affinity of palladium, platinum, iridium(IV) and osmium(IV) for the stationary phase.[14–16] Amberlite LA-1 hydrochloride seems a more promising liquid anion–exchanger for this purpose,[17,18] but the separation of the chloride complexes of palladium and platinum is unsatisfactory owing to the small differences between their R_F values, and elongated spots are obtained in paper chromatography. A better separation of Pd and Pt is achieved by paper or thin-layer chromatography on supports treated with a mixture of Amberlite LA-1 hydrochloride and tributyl phosphate,[19] but with this system it is impossible to separate iridium from other metals owing to the partial reduction of iridium(IV) to iridium(III) during development with solutions of hydrochloric acid, and iridium(III) forms a single zone with rhodium(III), moving with the solvent front in all chromatographic systems investigated.

The mixtures of eluting agents which are often useful in column ion-exchange separations of metal ion mixtures have been applied in extraction paper chromatography only for some metals in thiocyanate systems.[20–24] It is well known that alkylammonium cations have stronger affinity for nitrate than for chloride;[25,26] the possibility of altering, by addition of nitric acid to the eluent, the R_F values for platinum metals strongly extracted by TOA or quaternary alkylammonium salts, was investigated in the present work. Additionally, the possibility of utilization of paper chromatographic data for column extraction chromatographic separation of the mixture Rh–Pd–Pt with an analogous system was also investigated.

EXPERIMENTAL

Materials

Amberlite LA-1 (Schuchardt, F.R.G.), tri-n-octylamine (Koch-Light, England) and Aliquat 336 (tricaprylmethylammonium chloride; General Mills Chemicals, Inc., U.S.A.) were used as the extractants without further purification. Tri-n-octylbutylammonium nitrate containing 95%

of quaternary ammonium salt was prepared in the manner described previously.[27] The following noble metal compounds, of analytical grade, were used: H_2PtCl_6 30% solution (Mennica Panstwowa, Poland), $(NH_4)_2OsCl_6$ (Johnson-Matthey, England), $PdCl_2$ (POCh, Poland), Na_2IrCl_6 (Pfaltz-Bauer, F.R.G.), $(NH_4)_3IrCl_6$ (Johnson-Matthey, England). The $RhCl_3$aq. (Fluka, Switzerland) and platinum—rhodium alloy containing 10% Rh (Mennica Państwowa, Poland) were of pure grade.

Solutions of noble metals

The samples were usually in the form of 1% w/v noble metal solutions in 6*M* hydrochloric acid. The platinum content was determined gravimetrically[28] and rhodium cerimetrically.[29] More dilute solutions for determination of detection limits were prepared by dilution with a mixture of hydrochloric and nitric acids ($c_{HCl} = 4.5M$; $c_{HNO_3} = 2M$). The platinum–rhodium alloy (18.4 mg) was dissolved in *aqua regia* by heating for 5 hr on the water-bath. The solution was evaporated almost to dryness and the residue treated with 1.5 ml of conc. hydrochloric acid, evaporated again and diluted with conc. hydrochloric acid to a volume of 1.5 ml; 1 ml of this solution contained 1.24 mg of rhodium and 11.44 mg of platinum.

Paper chromatographic procedure

Xylene solutions (0.1*M*) of Aliquat 336, tri-n-octylbutylammonium nitrate and tri-n-octylamine or Amberlite LA-1 salts were used as impregnating solutions. TOA and Amberlite LA-1 were converted into their salts by shaking a 0.1*M* solution of the free base with an equal volume of *aqua regia* diluted 1:8 with distilled water, separating the phases and filtering the organic phase through cellulose. Whatman No. 4 paper strips were passed through the organic solution three times and pressed between two sheets of paper in order to remove the excess of impregnating solution. The paper strips were then air-dried to remove the diluent used for the liquid anion-exchanger. Then 2-μl volumes of solutions of the metals investigated were spotted on the start line of paper strips and the spots were air-dried. Aqueous nitric acid solutions and mixtures of nitric and hydrochloric acids were used as developing solutions. Descending development over a distance of 16 cm required 45–55 min, depending mainly on the acid concentration in the mobile phase.

After development, the paper was air-dried and the metals were detected by spraying the chromatograms with solutions of suitable reagents: 5% stannous chloride in 2*M* hydrochloric acid (Pt, Pd, Au, Rh), followed by 5% potassium iodide in water (Pt, Pd, Au, Rh, Os) or 1% ceric sulphate in water [Ir(III)]. The yellow spots from iridium(IV) were visible on the unsprayed chromatograms.

The detection limits were determined on paper strips treated with Aliquat 336 and eluted with an acid mixture ($c_{HCl} = 4.5M$; $c_{HNO_3} = 2M$) and found to be 0.25 μg (125 ppm of metal in the sample) for Pd, Pt and Au, 0.5 μg for Ir(IV) and Rh and 1 μg for Os(IV). If the concentration is lower than the detection limit, a larger sample should be taken by repetitive spotting. The length of the spot after chromatography depends on the concentration of the sample solution and was found to vary for platinum from 14 mm (250 ppm) to 33 mm (10^4 ppm) and for iridium(IV) from 12 mm (250 ppm) to 17 mm (6×10^3 ppm). It was also found that the spot corresponding to iridium(III) was not formed even when 12 μg of iridium(IV) were placed on the start line.

The volumes of stationary and mobile phases [determined on the basis of the weights of paper strips (*a*) unimpregnated, (*b*) impregnated with TOA salts and (*c*) developed with a mixture of hydrochloric and nitric acids ($c_{HCl} = 2.25M$; $c_{HNO_3} = 3M$)] were found to be 0.0906 ml and 2.93 ml, respectively, so the volume ratio of mobile to stationary phase in the paper chromatography was 32.4.

Column chromatographic procedure

Glass tubes (8.2 × 300 mm) were used in this work. Silica gel (0.05–0.2 mm), analytical grade (Merck, F.R.G.), was used as the support for the stationary phase. Tri-n-octylamine was converted into salt form by shaking a 0.4*M* TOA solution in chloroform with an equal volume of a mixture of hydrochloric and nitric acids ($c_{HCl} = 2.25M$; $c_{HNO_3} = 2M$). After separation of the phases, the organic phase was filtered through a cellulose filter and 50 ml of the solution were mixed with 40 g of silica gel. The diluent was then evaporated with a vacuum evaporator (Quickfit) on a water-bath. The coated support remained a white, free-flowing powder containing 0.165 g (0.2 ml) of amine salt/g. The dried support (10 g) was then slurried with 40 ml of the eluent ($c_{HCl} = 2.25M$; $c_{HNO_3} = 3M$), poured into the column, and covered with a Whatman No. 4 cellulose filter. The column height was 250 mm, the dead volume 0.4 ml, the organic phase volume 2 ml and the mobile phase volume 10 ml (determined from the retention volume for nickel, which is not retained). After the column had been washed with 10 ml of the first eluent, 0.6 ml of a synthetic mixture containing 1.98 mg of platinum(IV), 0.995 mg of palladium(II) and 1.033 mg of rhodium(III) in hydrochloric and nitric acids ($c_{HCl} = 2.25M$) $c_{HNO_3} = 3M$) was introduced into the column. Two-step elution under hydrostatic pressure (head of 250 mm) was used for the separation, 1-ml fractions being collected by a fraction collector equipped with a drop-counter. The whole elution needed 280 min at a flow-rate 0.4 ml/min.

Palladium and platinum were determined in single fractions by AAS, with a single-beam (Pye-Unicam) SP 192 atomic-absorption spectrometer. Rhodium was determined in individual fractions or in the total rhodium eluate spectrophotometrically at 500 nm; the calibration graph was based on rhodium(III) solutions in the mixture of acids used as the first eluent.

RESULTS AND DISCUSSION

The R_F values in laminar extraction chromatography depend mainly on the nature of both the organic and aqueous phases. The platinum metals have hitherto been separated on supports treated with Amberlite LA-1 hydrochloride, tributyl phosphate or mixtures of both, and developed with hydrochloric acid. From liquid–liquid extraction data it is known that tertiary long-chain alkylamines and quaternary alkylammonium salts are more selective than primary or secondary high molecular-weight amines[30,31] as extractants for platinum metals in hydrochloric acid. Paper or thin-layer chromatography experiments in chloride, bromide, iodide and thiocyanate systems have indicated that the halide complexes of platinum(IV), palladium(II), iridium(IV) and osmium(IV) are too strongly extracted by tertiary amine salts to permit their separation even at high concentrations of hydrohalic acids in the mobile phase.[14–16,32–34] It is known that decreasing the concentration of extracting agent in the impregnating solution decreases the capacity of the extractant and that at concentrations of extracting agents lower than 0.05*M* elongated spots are usually formed, even with microgram quantities of metals. The other way to alter R_F values is to change the composition of the aqueous mobile phase. Therefore, we first tried to use nitric acid solutions as non-complexing eluents for the platinum metals,

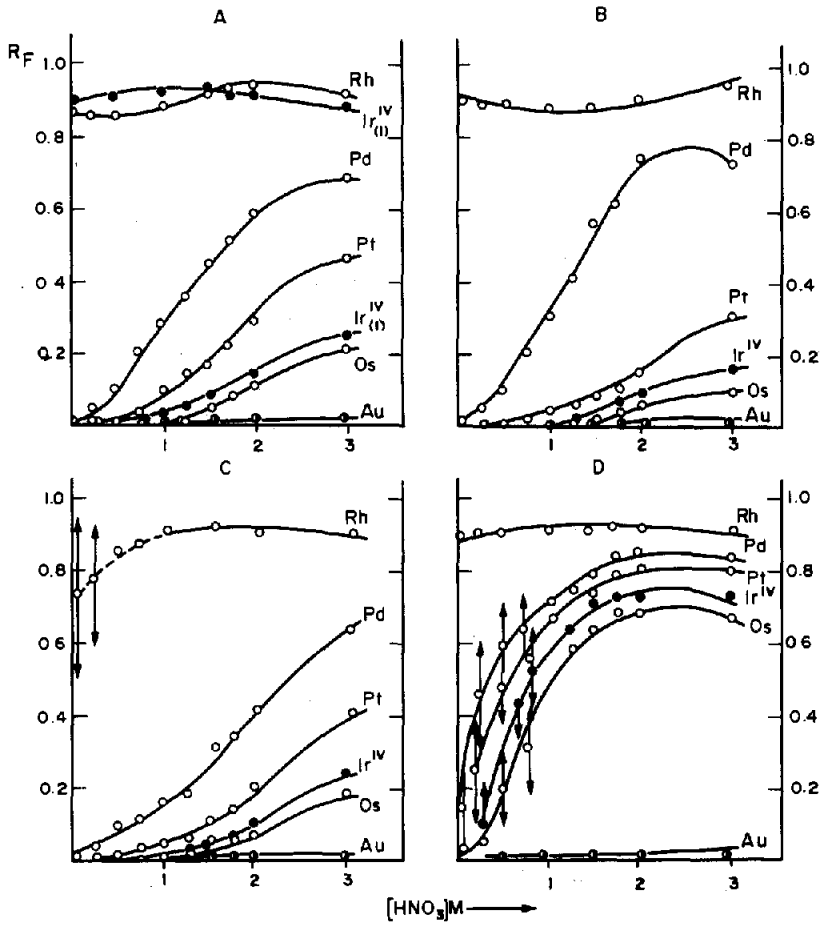

Fig. 1. R_F values of gold(III), osmium(IV), iridium(IV), platinum(IV), palladium(II), rhodium(III) and iridium(III) *vs.* HNO_3 concentration in the developing solution. Constant concentration of HCl = 2.25*M*. Stationary phases: A—TOA hydrochloride, B—Aliquat 336, C-tri-n-octylbutylammonium nitrate, D—Amberlite LA-1 hydrochloride.

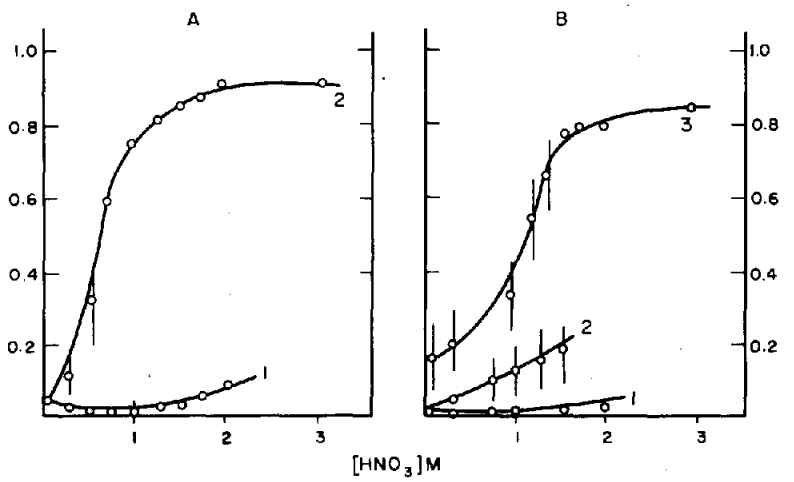

Fig. 2. R_F values of ruthenium(III) *vs.* concentration of HNO_3. Constant concentration of HCl = 2.25*M*. Stationary phases: A—TOA hydrochloride, B—Aliquat 336.

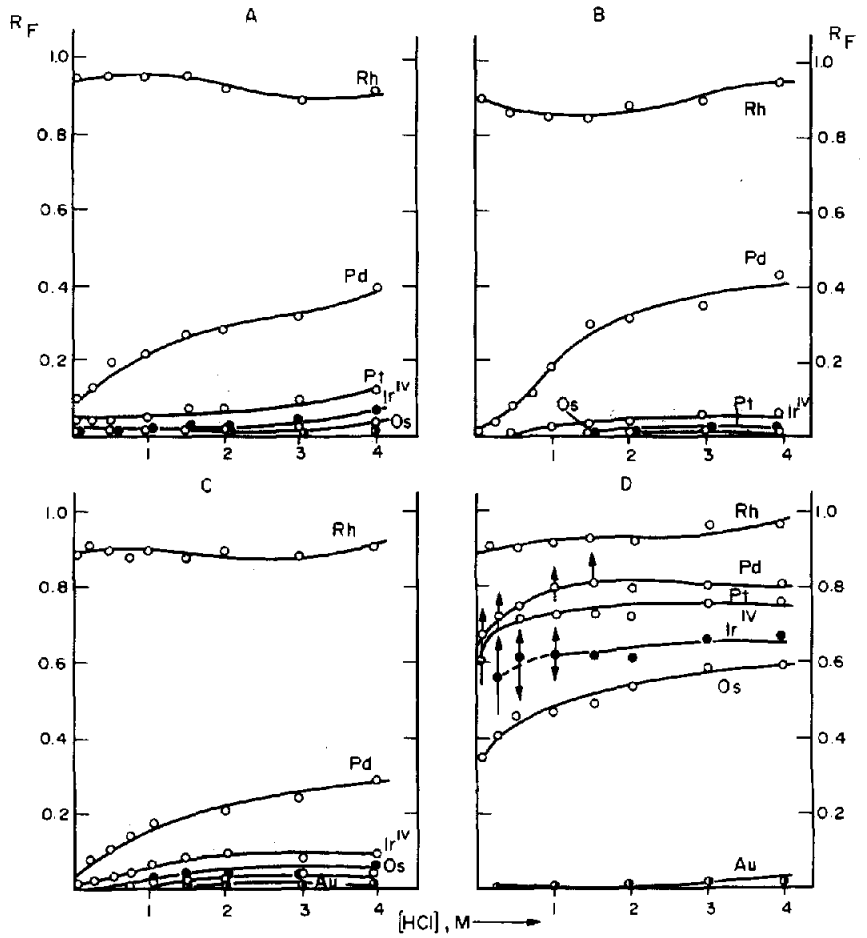

Fig. 3. R_F values of noble metals *vs.* HCl concentration in the mobile phase. Constant HNO_3 concentration = 1*M*. Designations as in Fig. 1.

but they proved unsuitable because elongated spots (comets) were obtained for palladium, platinum and iridium. These are probably due to partial hydrolysis of the chloride complexes of these metals to give aquo-chloro-complexes or hydroxy-chloro-complexes in the absence of chloride ions in the aqueous phase.[1] Double or triple spots were produced by iridium(III), one of which had the R_F value corresponding to iridium(IV). It seems that iridium(III) is partially oxidized to iridium(IV) during the development with nitric acid.

Earlier experiments using the moist paper technique with paper strips impregnated with diluted *aqua regia* and developed with solutions of liquid anion-exchangers in organic diluents, had indicated the possibility of separation of some platinum metals in this chromatographic system.[27] Therefore, we decided to try mixtures of hydrochloric and nitric acid as eluents in the extraction chromatography; the concentrations of the acids in the mobile phase were therefore systematically varied (Figs. 1–5). The results indicated that both acids have a significant influence. Only gold(III) and silver remain at the starting line in all the systems investigated, and rhodium(III) and copper(II) are not extracted and move with the solvent front. Ruthenium(III) forms double spots on paper strips treated with TOA or Aliquat 336 (see Fig. 2) whereas only one spot, moving with the solvent front, is found when Amberlite LA-1 is used as extractant. It seems that at least two complexes of ruthenium are present in the aqueous phase at low chloride concentrations and that only one of them is extracted by TOA or quaternary alkylammonium salts, but neither by Amberlite LA-1.

Iridium(III) is partially oxidized by nitric acid and forms two or three spots, the spot of lowest R_F value corresponding to iridium(IV). On the other hand, only one spot is obtained for iridium(IV) when the nitric acid concentration in the eluent exceeds 1*M* (Fig. 1), in contrast to the result for iridium(IV) in the chloride system.[19] With a constant nitric acid concentration of 1*M* and hydrochloric acid concentrations exceeding 2*M*, a second and just visible spot was formed (on paper strips treated with Aliquat 336 only), having an R_F value corresponding to iridium(III). Similar behaviour of iridium(IV) was also

observed when diluted *aqua regia* was used as mobile phase (Fig. 5), if the total concentration was lower than 1.6*M*; the iridium(IV) was partially reduced to iridium(III), which is not extracted by liquid anion-exchangers. From the results reported for iridium it is evident that the extraction coefficients obtained in various laboratories under somewhat different experimental conditions in batch extraction of this metal by high molecular-weight amines from aqueous hydrochloric acid are often not comparable, since in such experiments the total amount of iridium is usually determined in the aqueous or the organic phase and the oxidation state of the metal is not taken into consideration.[25] On the other hand, the double or triple spots often observed for iridium(IV) in other chromatographic systems[6,35,36] with hydrochloric acid present in the eluent, make the separation of the non-volatile noble metals difficult. Thus the use of mixtures of hydrochloric and nitric acids as eluents in the extraction chromatography of noble metals seems to be useful owing to formation of a single spot for iridium(IV) if the nitric acid concentration is sufficient to prevent reduction of this species.

The R_F values for palladium(II), platinum(IV), osmium(IV) and iridium(IV) increase with increasing concentration of both acids in the developing solution, independent of the liquid anion-exchanger used as stationary phase. The chromatographic results confirm the suggestion that Amberlite LA-1 gives not only the poorest extraction for platinum metals but also the lowest selectivity in comparison with other liquid anion-exchangers used as a stationary phase. At constant concentration of impregnant, and of acid mixture in the mobile phase, the R_F values of platinum(IV), iridium(IV) and osmium(IV) vary with the extractant, increasing in the extractant order Aliquat 336 < tri-n-octylbutylammonium nitrate < TOA < Amberlite LA-1. In contrast, palladium(II) is more strongly extracted by TOA than by Aliquat 336. Sharper separation of the pair Pd–Pt is obtainable on paper strips treated with Aliquat 336, but TOA or tri-n-octylbutylammonium nitrate can also be successfully used for separation of the non-volatile noble

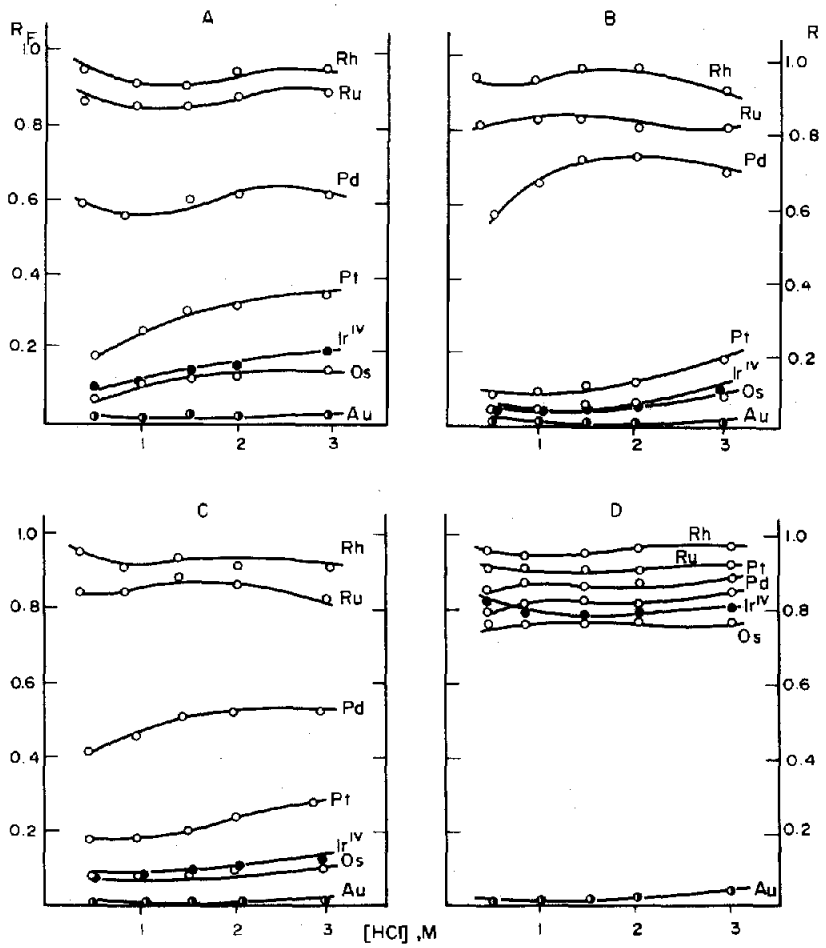

Fig. 4. R_F values of noble metals *vs.* HCl concentration in the mobile phase. Constant HNO_3 concentration = 2.25*M*. Designations as in Fig. 1.

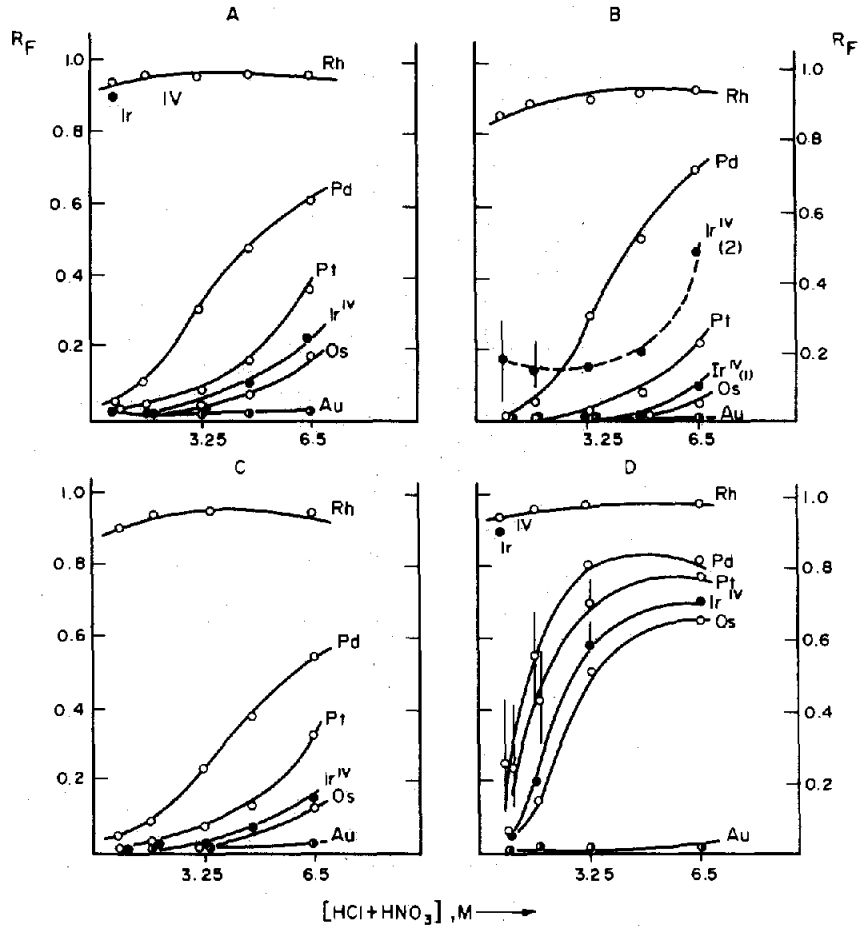

Fig. 5. R_F values of noble metals *vs.* total concentration of HCl and HNO_3 in the mobile phase (obtained by dilution of *aqua regia* with distilled water). Designations as in Fig. 1.

metals if the nitric acid concentration in the mobile phase is high enough, preferably > 1*M*. The affinity of the metals for the stationary phases decreases in the order Au(III) > Os(IV) > Ir(IV) > Pt(IV) > Pd(II) > Ru(III) > Rh(III) ~ Ir(III).

The dependence of R_F on the concentration of nitric or hydrochloric acid (compare Fig. 1 with Figs. 3 and 4) indicates the distinctly stronger eluting properties of nitric acid for platinum metals owing to the affinity of nitrate for the stationary phase being higher than that of chloride.[37,38] The extraction of the platinum metals in the chromatographic systems investigated can thus be described by

$$2(Am^+X^-)_o + MeCl^{2-}_{n+2} \rightleftharpoons [(Am^+)_2MeCl^{2-}_{n+2}]_o + 2X^-$$

where Am^+ denotes the alkylammonium cation and X^- is Cl^- or NO_3^-.

The R_F values in the chromatographic systems investigated and the low dependence of the length of spot on amount of metal offer several possibilities for separating various mixtures of non-volatile noble metals, and some of the separations performed are demonstrated in Figs. 6–8 for synthetic mixtures (containing 1 μg of each metal ion); the qualitative analysis for platinum–rhodium alloy was also successfully performed.

Recommended paper chromatographic procedure

Treat 50 mg of solid sample with 10 ml of *aqua regia* and heat on the water-bath to dissolve, or use an appropriate volume of a liquid sample. Evaporate the solution almost to dryness, add a few ml of concentrated hydrochloric acid and evaporate again. Dissolve the residue and make up to 5 ml with concentrated hydrochloric acid. Spot 2 μl of this solution on a paper strip impregnated with 0.1*M* Aliquat 336 or tri-n-octylamine salt in xylene and dry it. Develop the chromatogram with a mixture of hydrochloric and nitric acids (c_{HCl} = 4.5*M*; c_{HNO_3} = 2*M*) over a distance of 16 cm, dry the paper with a stream of hot air and spray first with 5% stannous chloride in 2*M* hydrochloric acid and then with 5% potassium iodide in water. Control experiments with synthetic solutions containing known amounts of noble metals are recommended. If the concentration of the metal ions in the test solution is lower than the detection limits, a bigger sample must be taken by multiple spotting.

The chromatographic systems recommended

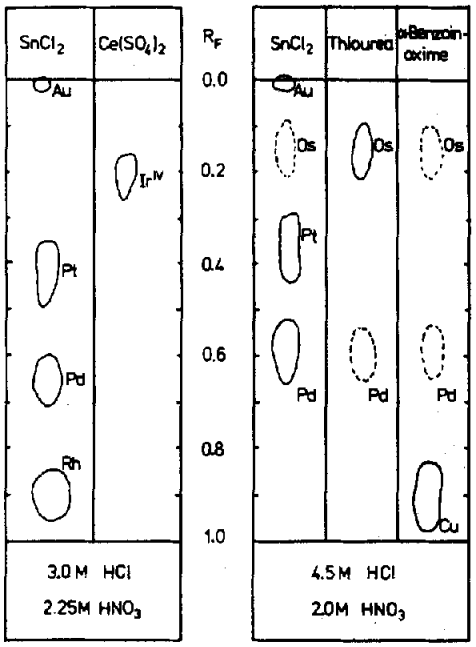

Fig. 6. Examples of chromatographic separation of noble metals on paper strips treated with TOA hydrochloride. The spots were visible after the chromatograms had been sprayed with the reagents mentioned in the upper part of the figure.

(except paper strips treated with Amberlite LA-1) are unsuitable for the separation of osmium and ruthenium; however, these metals can be successfully separated on paper strips treated with tributyl phosphate and developed with 6*M* hydrochloric acid.[18]

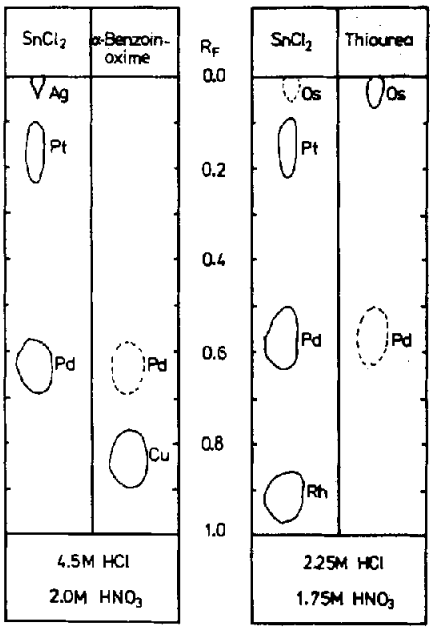

Fig. 7. Examples of chromatographic separation of noble metals on paper strips treated with Aliquat 336.

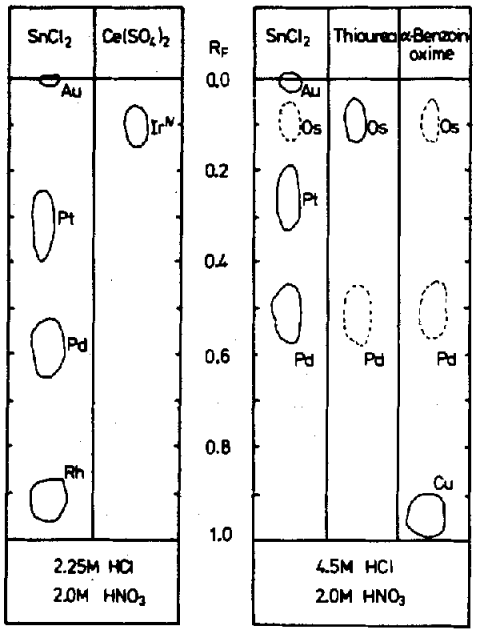

Fig. 8. Examples of chromatographic separation of noble metals on paper strips treated with tri-n-octylbutylammonium nitrate.

The systems proposed require comparatively short developing times (not exceeding 1 hr) owing to the relatively low concentration of acid in the mobile phase.

The results can also be useful in choosing the optimal conditions for column separation of the noble metals because the R_F values are correlated with the retention volumes (v_R) in column chromatography (under analogous experimental conditions) by the following equation[39]

$$\frac{v_R}{v_m} - 1 = \frac{A_m v_s}{A_s v_m}\left(\frac{1}{R_F} - 1\right) = k\left(\frac{1}{R_F} - 1\right)$$

where v_m and v_s denote the volumes of the mobile and stationary phases in the column, respectively, and A_m and A_s are the cross-sectional areas of the mobile and stationary phases in paper chromatography, respectively. In our chromatographic experiments with use of tri-n-octylamine salts as the stationary phase and a mixture of hydrochloric and nitric acids ($c_{HCl} = 2.25M$; $c_{HNO_3} = 3M$) as eluents, the ratios of A_m/A_s and v_s/v_m were found to be 32.4 and 0.2, respectively, so the coefficient k was 6.5. The retention volumes for rhodium and for platinum calculated from the paper chromatographic data and determined in column chromatography, as well as the separation factors for the pair Pd–Rh, are collected in Table 1. An example of column separation of the synthetic mixture containing milligram quantities of platinum, palladium and rhodium is given in Fig. 9. Table 2 reports the results of the determination of these metals (platinum and palladium were determined in single fractions, rhodium was determined in the total

Table 1. Comparison of experimental retention volumes and separation factors S_F for the pair Pd–Rh with those calculated from independent paper chromatographic experiments

	Eluent	Paper chromatography R_F	Paper chromatography $V_{R(calc)}$, ml	Paper chromatography S_F	Column chromatography $V_{R(exp)}$, ml	Column chromatography S_F	$\frac{V_{R(exp)}}{V_{R(calc)}}$
Rh	2.25*M* HCl, 3*M* HNO_3	0.95	13.6	8.9	16	8.8	1.2
Pd		0.68	41		63		1.5
Pd	2.25*M* HCl_1, 2*M* HNO_3	0.58	59.2		88		1.5

Table 2. The determination of rhodium, palladium and platinum after the separation of the synthetic mixture by column chromatography

	Added, *mg*	Found, *mg*
Rh(III)	1.04	1.03
Pd(II)	0.99	0.97
Pt(IV)	1.98	2.01

rhodium eluate). The reported column chromatographic results seem to be promising, so the paper chromatographic data included in this work should be useful in planning column separations of various metal–ion mixtures in analogous chromatographic systems.

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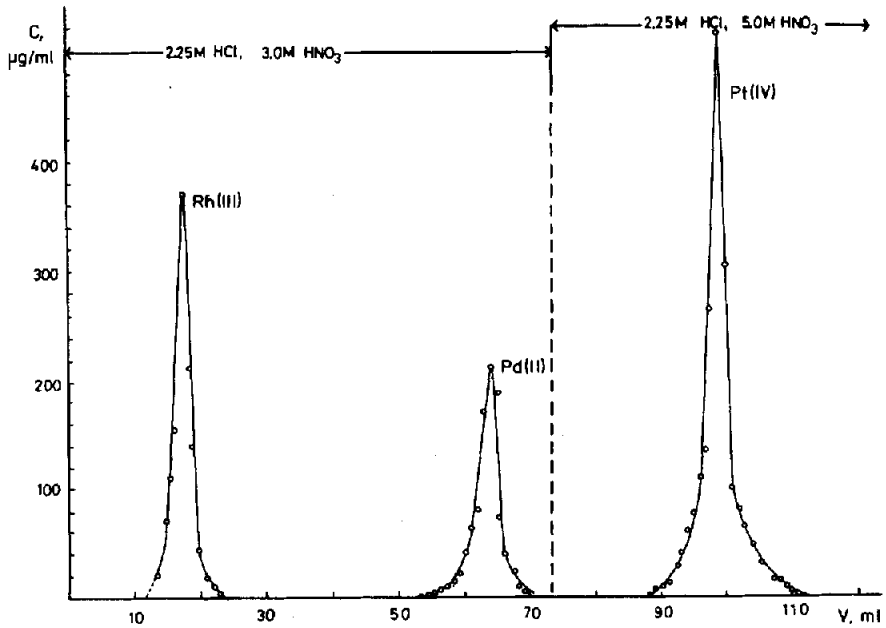

Fig. 9. Separation of Rh(104 μg), Pd(99 μg) and Pt(198 μg). Column: TOA-silica gel, 8.2 × 250 mm; flow-rate 0.4 ml/min.

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ACIDITES ET COMPLEXES DES ACIDES (ALKYL-et AMINOALKYL-) PHOSPHONIQUES—IV

ACIDES AMINOALKYLPHOSPHONIQUES $R^1R^2N(CH_2)_nCR^3R^4PO_3H_2$

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Résumé—Les acides étudiés diffèrent par la longueur de leur chaîne carbonée [$\overset{+}{N}H_3(CH_2)_nPO_3H^-$ avec $n = 1, 2, 3$], la substitution sur l'azote [$R^1R^2\overset{+}{N}HCH_2PO_3H^-$ avec $R^1 = H$; $R^2 = Me$, Et et $R^1 = R^2 = Me$, Et] ou l'encombrement sur le carbone porteur des groupements fonctionnels [$\overset{+}{N}H_3CR^3R^4PO_3H^-$ avec $R^3 = H$; $R^4 = Me$, Et, nPr, iPr, nBu et $R^3 = R^4 = Me$]. Les constantes d'acidité et les constantes globales de stabilité des complexes formés avec Mg(II), Ca(II), Co(II), Ni(II), Cu(II), Zn(II) sont obtenues à l'aide des programmes d'affinements multiparamétriques MUPROT et MUCOMP, appliqués aux données potentiométriques, obtenues à 25°, en milieu 0,1*M* en nitrate de potassium. Dans le cas le plus général, les espèces existantes sont MHA^+, MA, $M(OH)A^-$, MH_2A_2, MHA_2^- et MA_2^{2-} (A^{2-}: forme totalement ionisée du coordinat); l'examen préliminaire des résultats conduit à dégager certaines formes microscopiques prédominantes.

Un travail précédent a permis d'examiner, pour des acides alkylphosphoniques simples, la répercussion de l'acidité du groupement $-PO_3H_2$ sur son pouvoir complexant.[1] Nous avons entrepris, dès 1970, l'évaluation des constantes de stabilité des complexes formés par les acides $NH_2(CH_2)_nCR^3R^4PO_3H_2$ et divers cations parmi Mg(II), Ca(II), Co(II), Ni(II), Cu(II), Zn(II). L'influence de l'allongement de la chaîne carbonée ($R^3 = R^4 = H$; $n = 0, 1, 2$)[2–4] ou de sa ramification ($n = 0$; $R^3 = H$; $R^4 = Me$, Et, nPr, iPr, nBu) ($n = 0$; $R^3 = R^4 = Me$)[5] a été envisagée. Malheureusement, les méthodes de détermination utilisées alors étaient essentiellement basées sur l'exploitation graphique des données expérimentales. Or, cette technique aboutit à des résultats pouvant prêter à contestation et ceci d'autant plus que le nombre de constantes à déterminer est important. Depuis, nous avons réalisé des affinements multiparamétriques qui permettent d'obtenir des constantes d'acidité[6] et de stabilité[7] beaucoup plus fiables. Les valeurs antérieures ont donc été remises en question et soumises à ces ajustements; de plus, des constantes inédites, relatives aux espèces formées avec Mg(II), Ca(II) et certains des acides précédents, ont été déterminées.

Finalement, pour compléter la description du pouvoir complexant de ces composés, l'influence de l'encombrement sur l'azote est examinée, par l'intermédiaire des complexes cuivriques des acides $R^1R^2NCH_2PO_3H_2$ ($R^1 = H$; $R^2 = Me$, Et) ($R^1 = R^2 = Me$, Et).

PARTIE EXPERIMENTALE

Préparations

La plupart des acides aminophosphoniques sont des produits d'origine Calbiochem chromatographiquement purs et utilisés sans purification ultérieure.

Les acides *N*-méthylaminométhylphosphonique et *N*-éthylaminométhylphosphonique proviennent de l'amination de l'acide chlorométhylphosphonique[1] (0,1 mole), par un excès (0,4 mole) de l'amine primaire appropriée, en présence d'une solution de soude (0,3 mole). Il faut opérer en autoclave, vers 100° pendant environ 6 hr. L'évaporation de la solution conduit à un résidu sirupeux qui contient, en plus du composé attendu, les phosphonates $HOCH_2PO_3^{2-}$ et $RN(CH_2PO_3)_2^{4-}$. Le passage du mélange sur résine échangeuse d'ions H^+ permet d'éliminer ces sous-produits qui sont d'abord élués. L'éluat contenant l'acide est recueilli et concentré; l'addition d'éthanol permettant d'isoler l'acide (Rdt. 50–60%).

Les acides *N*,*N*-dialkylaminométhylphosphoniques sont préparés par la méthode proposée par Moedritzer et Irani[8] à partir d'amine secondaire, de formaldéhyde, d'acide orthophosphoreux en présence d'acide chorhydrique. On aboutit à un chlorhydrate d'acide qui est purifié, comme précédemment, par chromatographie sur échangeur d'ions H^+. Les acides sont obtenus par recristallisations dans des mélanges méthanol, acétate d'éthyle (Rdt. 80%).

L'analyse élémentaire de ces produits et leur dosage pHmétrique donnent des résultats en très bon accord avec ceux attendus.[9]

Neutralisations

Les données expérimentales (v, pH) sont obtenues à partir des neutralisations, par la potasse, à 25° en milieu de force ionique "constante",[1] des acides seuls et en présence de cations. La chaîne de mesure potentiométrique est standardisée par les tampons habituels. Le tableau 1 résume

Tableau 1. Récapitulation des conditions expérimentales[a] (force ionique[1] = 0,100 = $[KNO_3] + 3C_M^0$; température de 25°)

Acide XPO_3H_2 X=	Cations M^{2+} M=	C_A^0 constant	C_M^0 constant	Rapports C_A/C_M	Résolution du pH mètre	Résolution de la burette[b]
NH_2CH_2	Cu		2.10^{-3}	0,66; 1; 1,5; 2; 2,5; 3	0,005	0,01
$NH_2CH_2CH_2^s$	Mg, Ca, Co, Ni, Zn	4.10^{-3}		1; 2		
$NH_2CH_2CH_2CH_2^s$ NH_2CHMe^c NH_2CHBu NH_2CHiPr NH_2CMe_2 $MeNHCH_2$	Cu		10^{-3}	0,66; 1; 1,5; 2; 2,5; 3	0,005	0,005
	Mg, Ca[d]	2.10^{-3}		0,2; 0,5; 1		
$EtNHCH_2$ Me_2NCH_2 Et_2NCH_2	Cu	$1,5.10^{-3}$		2; 3	0,001	0,005

Remarques. [a] Les acides non mentionnés n'ont donné lieu qu'à des études de constantes d'acidité. [b] La précision sur le volume est toujours meilleure que la résolution indiquée. [c] Les solutions à neutraliser sont préparées par pesée d'acide et non à partir d'une solution stock. [d] Uniquement dans le cas de l'acide amino-3 propylphosphonique.

les conditions opératoires: pour plus de détails, ainsi que pour la description des courbes de neutralisation obtenues, nous renvoyons aux publications antérieures.[2-5] Cependant nous apporterons quelques compléments relatifs aux précipitations. Il a été vu que les acides phosphoniques forment généralement des phosphonates basiques insolubles $RPO_3Cu.yCu(OH)_2$.[1] Cette précipitation est nettement retardée chez les acides aminophosphoniques mais elle subsiste toujours et correspond encore à un hydroxyphosphonate qui s'enrichit en $Cu(OH)_2$ lorsque le pH croît. Dans les mélanges de Cu(II) et d'acides amino-1 alkylphosphoniques comportant un excès de complexant ($C_A/C_M \geq 2$) la précipitation est imperceptible. Il en va différemment pour les composés substitués sur l'azote où l'apparition de sel basique est d'autant plus avancée que l'encombrement sur l'azote est important: par exemple, avec

Tableau 2. Constantes de stabilité des complexes de l'acide aminométhylphosphonique $\overset{+}{N}H_3CH_2PO_3H^-$ (H_2A), à 25°, en milieu KNO_3 0,1*M*

qjp	Espèces	log $\beta_{q/p}(3\sigma)$	Littérature		
			[e]	[f]	[g]
011	HA^-	10,05 (0,02)	10,0	9,97	9,86
021	H_2A	15,44 (0,01$_5$)	15,35	15,29	15,15
031	H_3A^+	15,88	17,2		
111	$MgHA^+$	11,38 (0,02)			
101	MgA	2,03 (0,03)			
111	$CaHA^+$	11,14 (0,03)			
101	CaA	1,71 (0,04)			
111	$CoHA^+$	11,79 (0,02)			12,73
101	CoA	4,45 (0,04)			4,78
122	CoH_2A_2	a			
112	$CoHA_2^-$	16,75 (0,1)			
102	CoA_2^{2-}	8,09 (0,05)			8,79
111	$NiHA^+$	11,69 (0,07)			12,75
101	NiA	5,29 (0,04)		4,94	4,90
122	NiH_2A_2	b			
112	$NiHA_2^-$	16,4 (0,6)			
102	NiA_2^{2-}	8,98 (0,05)		8,5	8,91
111	$CuHA^+$	12,56 (0,02)			13,25
101	CuA	8,12 (0,02)		7,77	7,85
1-11	$Cu(OH)A^-$	c			
122	CuH_2A_2	24,8 (0,2)			26,77
112	$CuHA_2^-$	20,20 (0,06)			
102	CuA_2^{2-}	14,65 (0,04)		14,1	14,06
111	$ZnHA^+$	11,72 (0,06)			12,72
101	ZnA	5,00 (0,08)			5,26
1-11	$Zn(OH)A^-$	d			
122	ZnH_2A_2	23,6 (0,3)			
					(ZnA_2^{2-}: 8,68)

a, b, c, d: avec la précision de nos mesures, la présence de ces complexes s'avère incertaine ($\sigma \sim \beta$); a ($\log \beta_{122} = 22,9$); b ($\log \beta_{122} = 22,6$); c ($\log \beta_{1-11} = -0,4$); d ($\log \beta_{1-11} = -1,9$).

[e]: μ variable ($C_A = 0,1$).[13] [f]: 25°, $\mu = 0,5$ ($NaClO_4$).[14] [g]: 25°, $\mu = 0,1$ ($NaClO_4$).[15]

Tableau 3. Constantes de stabilité des complexes de l'acide amino-2 éthylphosphonique $\overset{+}{N}H_3CH_2CH_2PO_3H^-$ (H_2A), à 25°, en milieu KNO_3 0,1*M*

qjp	Espèces[a]	$\log \beta_{qjp}(3\sigma)$	Littérature		
			[d]	[e]	[f]
011	HA^-	11,04 (0,03)	10,8	11,01	10,98
021	H_2A	17,285 (0,02)	17,8	17,98	17,27
031	H_3A^+	18,41	20,25	20,09	
111	$MgHA^+$	12,48 (0,07)			
101	MgA	2,13 (0,07)			
111	$CaHA^+$	12,22 (0,12)			
101	CaA	1,74 (0,13)			
111	$CoHA^+$	12,74 (0,07)			13,91
101	CoA	4,67 (0,06)			4,98
1-11	$Co(OH)A^-$[b]	−4,70 (0,06)			(CoA_2^{2-}: 8,07)
111	$NiHA^+$	12,80 (0,06)			13,90
101	NiA	5,20 (0,05)			5,69
122	NiH_2A_2	25,6 (0,5)			
112	$NiHA_2^-$	18,8 (0,2)			
102	NiA_2^{2-}[c]	10,1 (0,1)			10,50
111	$CuHA^+$	13,75 (0,04)			14,56
101	CuA	8,50 (0,02)			7,52
1-11	$Cu(OH)A^-$	1,04 (0,07)			
122	CuH_2A_2	27,1 (0,2)			29,20
112	$CuHA_2^-$	21,4 (0,2)			
102	CuA_2^{2-}	14,3 (0,5)			14,76
111	$ZnHA^+$	12,99 (0,08)			13,89
101	ZnA	6,16 (0,05)			6,36
1-11	$Zn(OH)A^-$	−1,70 (0,04)			
122	ZnH_2A_2	26,2 (0,2)			
					(ZnA_2^{2-}: 12,46)

[a] une décomposition, même faible, de l'acide de départ perturbe fortement les courbes de neutralisation.

[b] β_{1-11} peut être remplacé par β_{102} {$\log \beta_{102} = 8,5$ (0,3)}, mais l'écart-type σ_r est légèrement supérieur.

[c] β_{102} peut être remplacé par β_{1-11} {$\log \beta_{1-11} = -3,9$ (0,1)}. Dans les cas b et c, les paramètres β_{1-11} et β_{102} sont très fortement corrélés.

[d] μ variable ($C_A = 0,1$).[16] [e] conditions non précisées.[17] [f] 25°, $\mu = 0,1$ ($NaClO_4$).[15]

l'acide *N*,*N*-diméthylaminométhylphosphonique une précipitation est decelée pour $C_A/C_M = 2$; pH = 7,2; taux de neutralisation = 1,6, tandis qu'elle se produit beaucoup plus tôt avec l'acide *N*,*N*-diéthylaminométhylphosphonique ($C_A/C_M = 2$; pH = 6,6; taux de neutralisation = 1,1) rendant alors difficile l'étude des complexes. L'augmentation de la chaîne carbonée des acides ω-aminoalkylphosphoniques diminue l'acidité des solutions: lorsque le nombre d'atomes de carbone croît, la précipitation interfère pour des taux de neutralisation plus faibles.

Tableau 4. Constantes de stabilité des complexes de l'acide amino-3 propylphosphonique $\overset{+}{N}H_3CH_2CH_2CH_2PO_3H^-$ (H_2A), à 25°, en milieu KNO_3 0,1*M*

qjp	Espèces[a]	$\log \beta_{qjp}(3\sigma)$	Littérature
			[b]
011	HA^-	11,065 (0,04)	10,55
021	H_2A	17,95 (0,03)	17,40
031	H_3A^+	19,58	
111	$MgHA^+$	12,57 (0,05)	
101	MgA	2,01 (0,08)	
111	$CaHA^+$	12,37 (0,05)	
101	CaA	1,68 (0,07)	
111	$CuHA^+$	13,97 (0,05)	14,00
101	CuA	7,15 (0,2)	7,10
1-11	$Cu(OH)A^-$	0,1 (0,2)	
			(CuH_2A_2: 28,27)
			(CuA_2^{2-}: 13,47)

[a] des précipitations prématurées (hydroxydes, phosphonates) rendent les études des complexes difficiles (Cu^{2+}) ou impossibles (Ni^{2+}, Co^{2+}, Zn^{2+}...).

[b] 25°, $\mu = 0,1$ ($NaClO_4$).[15]

RESULTATS

Les tableaux 2 à 6 regroupent les constantes globales des stabilité $\beta_{qjp} = [M_qH_jA_p]/(m^q h^j a^p)$ obtenues à l'aide des programmes d'affinement MUPROT[6] et MUCOMP.[7] Les domaines de confiance 3σ attribués aux β_{qjp} sont généralement plus importants que ceux des affinements classiques, vu le plus grand nombre de paramètres ajustés. Les constantes relatives aux complexes hydroxylés (espèce: log β_{qj0}) utilisées dans les calculs ont été déterminées [$Cu_2(OH)_2^{2+}$ −10,7; $MgOH^+$ −11,9$_5$] ou sont tirées de la littérature[10]

Tableau 5. Constantes de stabilité des complexes des acides amino-1 alkylphosphoniques $\overset{+}{N}H_3CR^3R^4PO_3H^-(H_2A)$, à 25°, en milieu KNO_3 0,1*M*

R^3	R^4	*qjp*	Espèces	log $\beta_{qjp}(3\sigma)$	Littérature	
H	Me	011	HA^-	10,195 (0,025)		
		021	H_2A	15,78 (0,015)		
		031	H_3A^+	16,25		
		111	$MgHA^+$	11,54 (0,06)		
		101	MgA	2,00 (0,08)		
		111	$CuHA^+$	12,82 (0,05)		
		101	CuA	8,50 (0,02)		
		1-11	$Cu(OH)A^-$	−0,1 (1)		
		122	CuH_2A_2	25,9 (0,4)		
		112	$CuHA_2^-$	21,0 (0,1)		
		102	CuA_2^{2-}	15,40 (0,04)		
H	Et	011	HA^-	10,255 (0,02)	10,28 [b]	
		021	H_2A	15,91 (0,01)	16,03	
		031	H_3A^+		17,98	
H	nPr	011	HA^-	10,285 (0,02)	10,32	
		021	H_2A	15,96 (0,01)	16,15	
		031	H_3A^+		18,10	
H	iPr	011	HA^-	10,355 (0,04)	10,45	
		021	H_2A	16,15 (0,02)	16,45	
		031	H_3A^+	16,77	18,49	
		111	$MgHA^+$	11,73 (0,06)		
		101	MgA	2,15 (0,05)		
		111	$CuHA^+$	13,71 (0,02)		
		101	CuA	9,47 (0,01)		
		1-11	$Cu(OH)A^-$	1,7 (0,3)		
		122	CuH_2A_2	26,7 (0,5)		
		112	$CuHA_2^-$	22,53 (0,06)		
		102	CuA_2^{2-}	17,32 (0,05)		
H	nBu	011	HA^-	10,29 (0,03)	10,35	
		021	H_2A	15,99 (0,02)	16,17	
		031	H_3A^+	16,57	18,00	
		111	$MgHA^+$	11,59 (0,07)		
		101	MgA	2,03 (0,05)		
		111	$CuHA^+$	13,25 (0,03)		
		101	CuA	8,97 (0,01)		
		1-11	$Cu(OH)A^-$	0,8 (0,7)		
		122	CuH_2A_2	25,9 (0,6)		
		112	$CuHA_2^-$	21,60 (0,08)		
		102	CuA_2^{2-}	16,27 (0,05)		
Me	Me	011	HA^-	10,31 (0,03)[a]	10,43	10,31 [c]
		021	H_2A	16,115 (0,02)[a]	16,48	16,16
		031	H_3A^+	16,67	18,57	17,81
		111	$MgHA^+$	11,62 (0,07)		
		101	MgA	2,01 (0,06)		14,39 [d]
		111	$CuHA^+$	13,68 (0,08)		8,47
		101	CuA	9,13 (0,03)		28,69
		122	CuH_2A_2	27,25 (0,2)		
		112	$CuHA_2^-$	22,32 (0,09)		
		102	CuA_2^{2-}	16,64 (0,05)		15,29

[a] un autre lot de cet acide donne log β_{011} = 10,27 et log β_{021} = 16,11. La précision des mesures est insuffisante pour pouvoir trancher. Les valeurs retenues sont relatives à l'acide utilisé pour l'étude des complexes.

[b] conditions non précisées.[17] [c] 25°, μ = 0,1 (KCl).[18] [d] 25°, μ = 0,1 (KCl).[19]

Tableau 6. Constantes de stabilité des complexes des acides *N*-alkylaminométhylphosphoniques $R^1R^2\overset{+}{N}H\ CH_2PO_3H^-$ (H_2A), à 25°, en milieu KNO_3 0,1*M*

R^1	R^2	*qjp*	Espèces	log $\beta_{qjp}(3\sigma)$	Littérature
H	Me	011	HA^-	10,912 (0,006)	
		021	H_2A	16,222 (0,005)	
		031	H_3A^+	16,86	
		111	$CuHA^+$	13,325 (0,01)	
		101	CuA	8,29 (0,02)	
		1–11	$Cu(OH)A^-$	0,09 (0,09)	
		122	CuH_2A_2	25,9 (0,15)	
		112	$CuHA_2^-$	20,98 (0,1)	
		102	CuA_2^{2-}	14,59 (0,03)	
H	Et	011	HA^-	11,005 (0,01)	
		021	H_2A	16,341 (0,008)	
		031	H_3A^+	16,87	
		111	$CuHA^+$	13,415 (0,01)	
		101	CuA	7,72 (0,02)	
		1–11	$Cu(OH)A^-$	0,15 (0,06)	
		122	CuH_2A_2	26,31 (0,04)	
		112	$CuHA_2^-$	20,73 (0,05)	
		102	CuA_2^{2-}	13,0 (0,2)	
Me	Me	011	HA^-	11,063 (0,009)	
		021	H_2A	16,247 (0,010)	
		031	H_3A^+	16,70	
		111	$CuHA^+$	13,36 (0,02)	
		101	CuA	7,99 (0,03)	
		1–11	$Cu(OH)A^-$	0,20 (0,07)	
		122	CuH_2A_2	26,08 (0,1)	
		112	$CuHA_2^-$	20,84 (0,1)	
		102	CuA_2^{2-}	13,84 (0,06)	
Et	Et	011	HA^-	11,81 (0,03)	10,32 [a]
		021	H_2A	17,088 (0,03)	18,11
		111	$CuHA^+$	14,12 (0,01)	
		110	CuA	7,46 (0,05)	
		1–11	$Cu(OH)A^-$	−0,02 (0,1)	
		122	CuH_2A_2	27,56 (0,09)	

[a] 25°, $\mu = 1(KNO_3)$.[20]

($CaOH^+$ −12,9; $CoOH^+$ −9,8; $NiOH^+$ −9,3; $ZnOH^+$ −9,8). Les constantes globales de formation de H_3A^+ (β_{031}) sont calculées à partir des constantes d'acidités moyennement fortes déterminées par ailleurs.[12]

Pour simplifier la lecture, les résultats obtenus par d'autres auteurs ont été mis sous forme de constantes globales β_{qjp}. Signalons d'autres déterminations non mentionnées dans les tableaux: elles concernent la complexation de Be(II)[18] et de divers cations[19] par l'acide amino-1 méthyl-1 éthylphosphonique, des alcalinoterreux par les acides amino-2 hydroxy-1 alkyl phosphoniques[21] et de Cr(III) par les acides amino-2 alkylphosphoniques;[22] des études chromatographiques,[23,24] conductimétriques et spectrophotométriques[24] ayant été menées sur les complexes des acides aminoalkylphosphoniques. La comparaison avec les valeurs de la littérature s'avère décevante. En effet, des divergences très importantes sont observées qui ne peuvent être uniquement imputées aux différences de force ionique ou au mode d'expression des constantes (constantes mixtes au lieu de constantes exprimées en concentrations). Leur explication se trouve dans les méthodes de détermination trop sommaires ou dans l'omission d'espèces non négligeables. Il se pourrait également que la pureté des produits soit en cause: elle serait alors capable d'expliquer les écarts observés sur les constantes d'acidité de l'acide amino-2 éthylphosphonique (tableau 3).

DISCUSSION

Le schéma microscopique de dissociation des acides aminophosphoniques est représenté sur la figure 1a. Les constantes d'acidité de l'acide triméthylammonium méthylphosphonique, qui est un zwitterion permanent ($Me_3\overset{+}{N}CH_2PO_3H^-$, log k_{011} = 5,099)[1] et de l'acide diméthylaminométhylphosphonique (log β_{021} − log β_{011} = 5,184) peuvent être considérées comme identiques, compte-tenu de la perturbation provoquée par le méthyle supplémentaire. Cette similitude indique sans ambiguïté que les acides aminophosphoniques sont sous forme dipolaire

$$(H_2A):H\overset{+}{N}—R—PO_3H^-$$

et qu'ils se dissocient pour former ensuite

$$\overset{|}{\overset{+}{H}}N—R—PO_3^{2-}(HA^-).$$

Les formes H_3A^+, HA^- et A^{2-} correspondent donc aux espèces microscopiques encadrées sur la figure 1a.

L'interaction d'un cation M^{2+} avec les formes symbolisées par HA^- et A^{2-} aboutit, dans le cas le plus général, à l'apparition des espèces MHA^+, $M(HA)_2$, $M(HA)A^-$, MA, MA_2^{2-} et $M(OH)A^-$. Nous examinerons plus particulièrement le cas des espèces MHA^+, MA et $M(OH)A^-$, les autres découlant de celles-ci par addition de motifs HA^- et A^{2-}.

Dans le complexe protoné MHA^+ la coordination s'effectue essentiellement par le groupement phosphonate (voir fig. 1b). Comme précédemment, ce choix découle de la comparaison de la stabilité des phosphonates $Me_3\overset{+}{N}CH_2PO_3Cu$ ($\log \beta_{011} = 2{,}18$)[1] et $Me_2\overset{+}{N}HCH_2PO_3Cu$ ($\log \beta_{111} - \log \beta_{011} = 2{,}30$): il fallait d'ailleurs s'y attendre étant donné qu'une proposition considérable de HA^- est sous forme de

$$\overset{|}{\overset{+}{H}}N—R—PO_3^{2-}.$$

Des complexes protonés ont été isolés et étudiés par diverses méthodes spectroscopiques:[25–28] il a été montré que dans ces espèces seuls les atomes d'oxygène du groupement phosphonate échangent des liaisons avec le métal, l'azote étant sous forme ammonium.

Le départ du proton fixé sur l'azote libère la fonction amine et conduit à des espèces du type MA. Ce complexe doit correspondre en réalité à la coexistence des deux formes microscopiques les plus probables: d'une part le chélate où la liaison azote–métal s'ajoute à la liaison phosphonate–métal et d'autre part l'espèce comportant une fonction amine libre (Fig. 1b). Ainsi, la stabilité des complexes des alcalino-terreux et de Ca(II) en particulier est peu améliorée lorsque l'on passe de la complexation par $-PO_3^{2-}$ seul ($1{,}09 < \log \beta_{111} - \log \beta_{011} < 1{,}31$; tableaux 2 à 4) à celle qui ajoute la fonction amine ($1{,}68 < \log \beta_{101} < 1{,}74$). La contribution de $-PO_3^{2-}$ à la stabilité est donc importante. En d'autres termes, MA doit correspondre à deux formes I et II (Fig. 1b), la forme I étant loin d'être négligeable. Ces observations permettent d'expliquer les résultats de Carter *et al.*[29] qui ont déterminé les constantes de stabilité des complexes de Ca(II) avec l'acide nitrilotri(méthylène phosphonique) ($\log \beta_{101} = 6{,}68$) et de son *N*-oxyde ($\log \beta_{101} = 5{,}69$). La faible atténuation de stabilité, non rencontrée chez les aminocarboxyliques correspondants, est explicable si l'on admet, en plus du chélate, l'existence d'une forme où l'azote est libre. Par contre, dans le cas des métaux de transition, un net regain de stabilité est observé lorsqu'on l'on passe de MHA^+ à MA (voir tableaux) traduisant l'intervention d'une liaison azote–métal avec formation d'un chélate (Fig. 1b, forme II). Des études spectroscopiques menées sur des complexes du type MA, ont mis en évidence que le métal était lié à la fois aux atomes d'oxygène du groupement phosphonate et à l'atome d'azote.[28,30] Une forme CuA, où l'amine

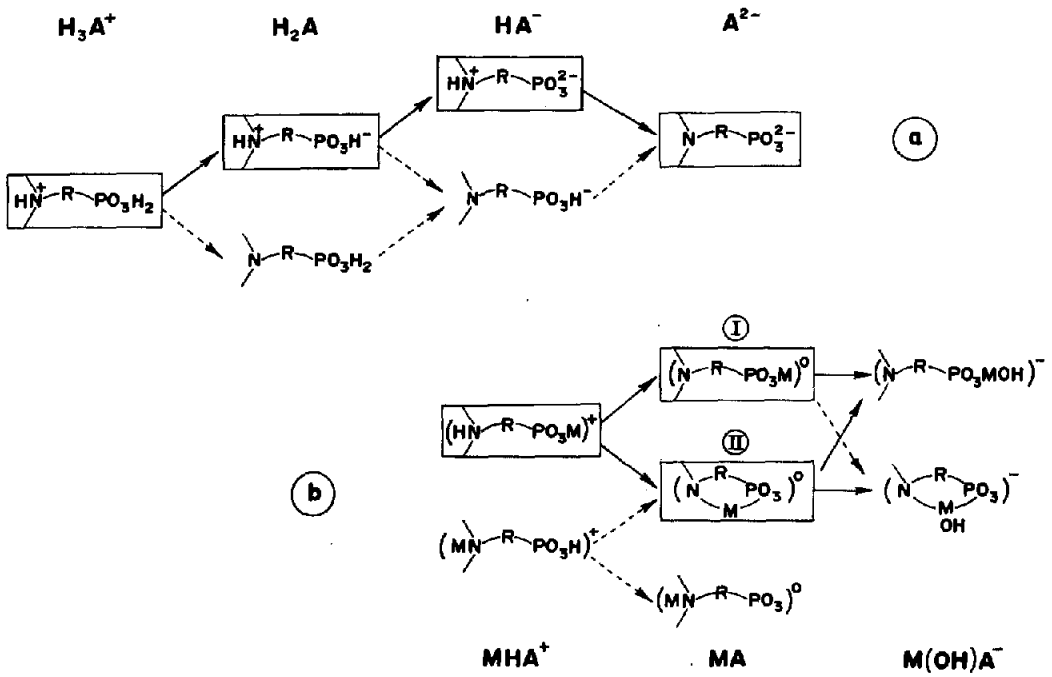

Fig. 1. Schémas microscopiques de dissociation des acides aminoalkylphosphoniques (*a*) et des complexes MHA^+, MA et $M(OH)A^-$ (*b*).

$-NH_2$ n'est pas liée au cuivre a été signalée par Jezowska-Trzebiatowska *et al.*[31] Cependant, vu le pH de travail (HCl 0,05*M*) la fonction amine doit être protonée: ces auteurs ont cru être en présence de CuA, alors qu'il doit s'agir de $CuHA^+$.

Evidemment, le complexe hydroxylé $M(OH)A^-$ résulte de la fixation d'un hydroxyle sur les formes MA précédentes (Fig. 1b). De plus, une rupture du chélate, résultant de la compétition entre l'oxygène de l'hydroxyle et l'azote, est concevable.

Les nombreuses constantes disponibles méritent évidemment une synthèse approfondie qui fera l'objet d'une publication particulière.

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Summary—The acids under study differed from one another in length of the carbon chain [$\overset{+}{N}H_3(CH_2)_nPO_3H^-$ for n = 1, 2, 3], substitution on the nitrogen atom [$R^1R^2\overset{+}{N}HCH_2PO_3H^-$ for R^1 = H; R^2 = Me, Et and $R^1 = R^2$ = Me, Et] or extent of branching on the carbon atom adjacent to functional groups [$\overset{+}{N}H_3CR^3R^4PO_3H^-$ for R^3 = H; R^4 = Me, Et, nPr, iPr, nBu and $R^3 = R^4$ = Me]. Acidity constants and overall stability constants of complexes formed with Ca(II), Mg(II), Co(II), Ni(II), Cu(II), Zn(II) were obtained with the multiparametric refinement programs MUPROT and MUCOMP, applied to potentiometric data, obtained at 25°, in a 0.1*M* potassium nitrate medium. In the most general case, the existing species are MHA^+, MA, $M(OH)A^-$, MH_2A_2, MHA_2^- and MA_2^{2-}, where A^{2-} stands for the fully ionized ligand; preliminary examination of results points out some predominant microscopic forms.

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EVALUATION OF ACID–BASE TITRATION CURVES OBTAINED BY THE TRIANGLE-PROGRAMMED TITRATION TECHNIQUE IN FLOWING SOLUTIONS

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Summary—Different evaluation techniques for triangle-programmed coulometric acid–base titration curves obtained with various detector systems are compared. In the case of potentiometric detection, hardware differentiation and linearization of the titration curves was investigated. Photometric end-point detection with single or mixed indicators was also studied. It was concluded that among the techniques studied the hardware potentiometric differentiation and the photometric detection with an indicator mixture are the most advantageous.

Many of the mechanized or automatic analysers carry out the determinations with flowing solutions. Most of the segmented or unsegmented flow analysers employ the relation between detector signal and concentration directly for evaluation of the results.[1–3] Ordinary titration to the end-point or the standard-addition method is only occasionally used.[4–6] The reliability of all these methods depends on the stability of the detectors used. It is commonly accepted that an analytical method using complete titration is much more reliable than a direct-relationship method. Recently efforts have been made in various laboratories to combine the simplicity and high rate of analysis of the flow methods with the advantages of the titrimetric methods. These efforts led us to introduce the so-called triangle-programmed titration technique, the theory[7,8] and practice[9–12] of which have been described.

The principle of the technique can be given shortly as follows.

The sample solution of constant concentration C_s is streamed in the flow-through analytical channel of the apparatus at a constant rate, V. At a certain point in the channel a selective reagent is introduced into the flow. After the reagent and sample streams have mixed, any cross-section of the mixed streaming solution is almost completely homogeneous. To carry out the determination a reagent addition-rate *vs.* time program with the shape of an isosceles triangle is used. That is, starting from zero, the reagent addition-rate V_R is increased according to the equation $V_R = nt$ where t = time ($0 < t \leqslant \tau$). After $t = \tau$ the reagent addition rate is decreased to zero according to the equation $V_R = (2\tau - t)n$.

As a result of the reagent-addition program, the reagent–sample mixture ratio in each infinitesimally thin segment of the streaming solution will be different. The fraction of reagent increases continuously as t increases from zero to τ and then it decreases again to zero. In this way the degree of titration first increases from segment to segment and then decreases. If an appropriate detector cell is placed in the flowing solution mixture, the degree of titration can be monitored. Since there is a delay before the infinitesimally thin solution segments of different degrees of titration reach the detector section, there will also be a time delay between achievement of a particular reagent addition-rate and the appearance of the corresponding detector signal. If the reagent addition-rate (V_R) well before the turning point $t = \tau$ exceeds the value which is stoichiometrically equivalent to the sample mass-flow (C_sV), then two separate segments will have a composition corresponding to 100% titration. The recorded detector-signal *vs.* time curve then appears as two titration curves connected to each other as mirror images; from the time period (Q) between the appearance of the equivalence points $t_E(1)$ and $t_E(2)$, the stoichiometry of the titration reaction, the parameters of the reagent addition program and the sample mass-flow, C_sV, the sample concentration can be calculated.

That is for the reaction

$$aS + bR = cP_1 + cP_2 \qquad (1)$$

$$C_s = \frac{2\tau - Q}{(a/bn).V} \qquad (2)$$

as shown elsewhere.[8] From the constants and the value of Q, C_s can be calculated, or it can be determined easily from Q and an appropriate calibration graph.

The coulometric variation of the triangle-programmed titration technique has already proved most satisfactory in practice and applicable to a variety

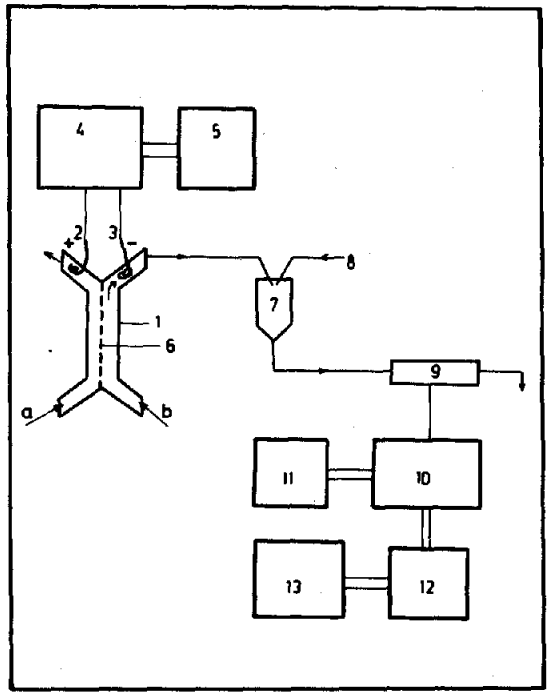

Fig. 1. Experimental set-up for triangle-programmed titrations with electrolytically generated reagents (for details, see text).

of analytical tasks. Various detectors and electrolytically generated titrants have been used in these studies. In continuing our work with this technique our aim is to work out appropriate simple automatic evaluation methods and apparatus, bearing in mind that some types of detector or titration reaction may create special problems in the location of the equivalence point. The aim of the present work was to investigate the applicability of various end-point location and evaluation methods in coulometric triangle-programmed acid–base titrations of flowing solutions.

EXPERIMENTAL

Apparatus

Several types of apparatus used in triangle-programmed titrations have been described in detail elsewhere.[9–12] Parts and units used earlier were employed in constructing the experimental set-up for the present studies.

A schematic view of the apparatus used is given in Fig. 1. The titrant (OH^- ions) was produced in an electrolysis cell (1) which contained two flow-through compartments (a,b) separated from each other. Two platinum-wire spirals (2), (3) served as generator electrodes and were connected to the output of a Radelkis type OH-405 current generator (4) controlled by a Philips type pM 5168 or PAR Model 175) programmer which produced the appropriate single triangle-shaped time program.

The two electrolysis half-cells were in electrical contact since in one section of the cell wall between them there was a window covered with dialysis membrane (6). Potassium nitrate solution (0.1 *M*) was pumped through the two half-cells by a peristaltic pump (LABOR MIM type OL-602). The solution stream passing compartment (a) was fed to waste while the stream leaving the cathodic compartment (b) entered a drip vessel (7) which served as a mixing chamber of small dead-volume. The sample stream (8) was pumped into the mixing chamber at constant rate with a peristaltic pump (LKB Varioperpex 12000). From the drip vessel the mixed stream of reagent-generation solution and sample was passed through the flow-through detector compartment (9) and overflowed to waste. The detector section (10) was provided with a Keithley Type 604 differential electrometer for potentiometric measurements and a Spekol Zeiss spectrophotometer for photometric measurements. A Radelkis type OH-814/1 recorder or occasionally an EMG type TR-1659 digital voltmeter (11), an interface (12) and an EMG type 666 computer (13) completed the apparatus.

Detectors

Three different kinds of detector were used, schematic drawings of which are shown in Fig. 2. The potentiometric detector (a) contains a microcapillary pH-sensitive glass electrode (14) (Radelkis type OP-7431) and a saturated calomel electrode (15): the differential potentiometric detector (b) is made of two microcapillary type glass electrodes and a delay coil (16) inserted between them; for the photometric measurements (c) a flow-through photometric cuvette was used as the detector section.

RESULTS AND DISCUSSION

Potentiometric methods

The theoretical titration curve obtained by the triangle-programmed titration method consists of two symmetrical curves as shown in Fig. 3. This curve results from titration of a strong acid. The left-hand part of the curve, sections A and B, is exactly the same as the conventional potentiometric titration curve. The potential jump gives the equivalence point,

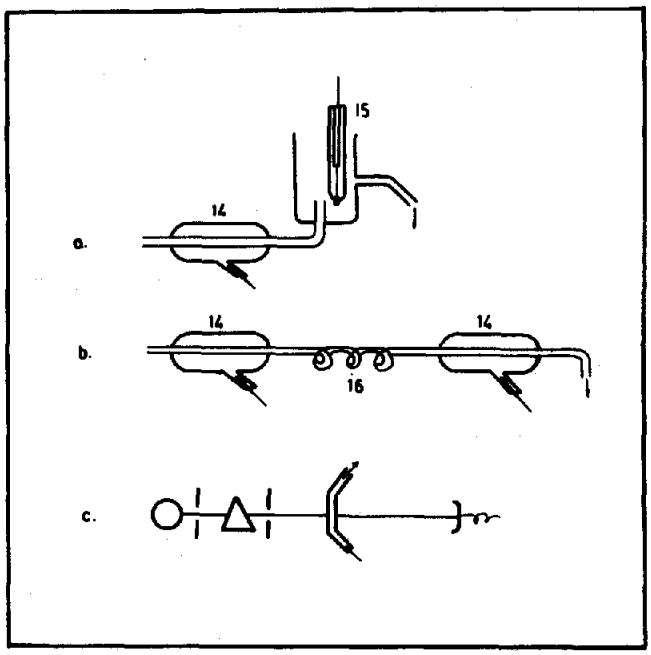

Fig. 2. Detectors used for the triangle-programmed titrations. a, Potentiometric detector. b, Differential potentiometric detector. c, Photometric detector.

i.e., the point where the flux of generated hydroxide ions is exactly the same as the flux of the acid to be determined. After the equivalence point the generating current still increases and the mixed stream contains an excess of hydroxide ions. Once its maximum is reached the generating current is decreased and the amount of generated hydroxide ions also decreases. The equivalence point will be passed again and after the generation program is over, the flow consists of the original acid solution. This second part of the curve, sections C and D, represents the titration of a strong base with a strong acid. The time Q elapsed between the two equivalence points $t_E(1)$ and $t_E(2)$ is linearly dependent on the concentration of the acid as described by equation (2). The experimentally obtained curve for titration of $1 \times 10^{-4}M$ hydrochloric acid is shown in Fig. 4. As can be seen, the curve is not strictly symmetrical. The part which rep-

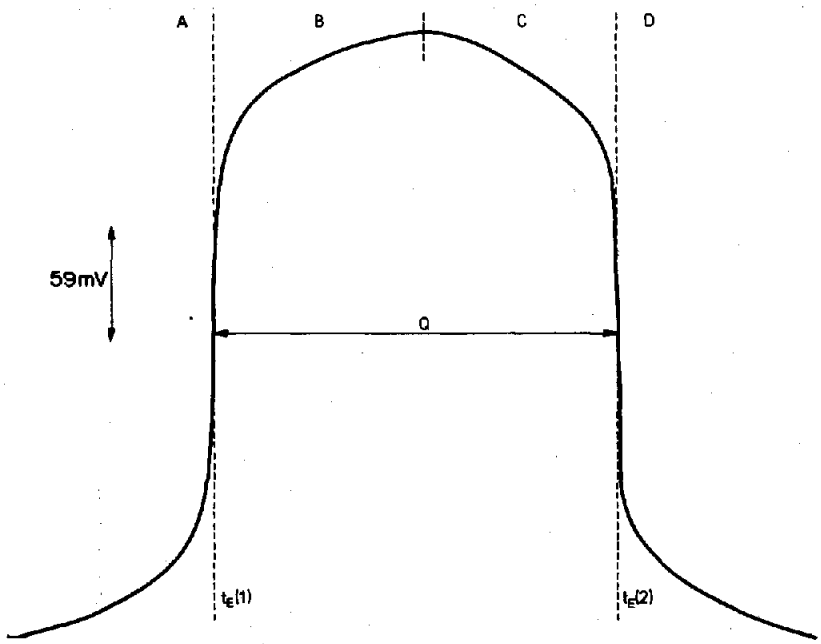

Fig. 3. Theoretical titration curve of a strong acid ($10^{-4}M$).

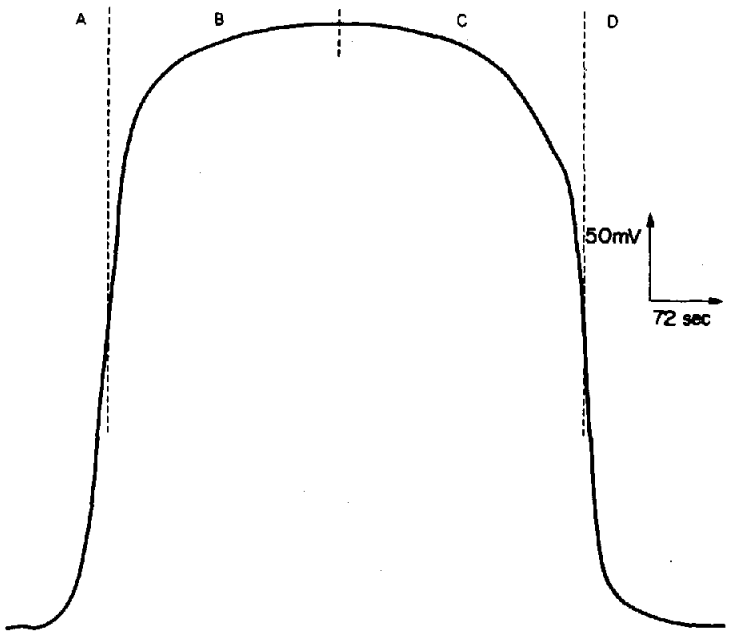

Fig. 4. Potentiometric triangle-programmed titration curve of $10^{-4}M$ hydrochloric acid. $i_{max} = 5$ mA; $2\tau = 130$ sec.

resents the titration of strong base with strong acid, sections C and D, is somewhat distorted because of tailing. Sometimes fluctuations in the measured potential can also be observed on the curve, and this is mostly due to electrical noise and incomplete mixing of the analyte and titrant before the measuring point. The disturbances caused by incomplete mixing can be overcome by employing a more effective mixer or by measuring the potential further away from the point of confluence, but unfortunately this can increase the tailing of the curve and also the time of the analysis.

The equivalence points can be obtained manually from the steepest parts of the potential jumps. However, various methods are available for the automatic evaluation of the titration curves.

Linear transformation of the titration curve

One numerical method for determining the equivalence point is the linear transformation of the titration curve. This method was first introduced by Sørensen[13] and later developed further by Gran[14] and Ingman and Still.[15] The derivation of the linear equation describing the course of the titration of any monobasic acid by the triangle-programmed titration method will be given.

The following equilibria exist in the system:

$$H^+ + A^- \rightleftharpoons HA \qquad K_{HA} = \frac{[HA]}{[H^+][A^-]} \tag{3}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_W = [H^+][OH^-] \tag{4}$$

where K_{HA} is the stability constant of the acid HA and K_w is the ionic product of water. The following balances can be written:

$$C_S = [HA] + [A^-] \tag{5}$$

$$V_R = nt = n([A^-] - [H^+] + [OH^-]) \tag{6}$$

$$V_S = C_S V \tag{7}$$

In the titration of monobasic acids, $a = b$ and at the equivalence point:

$$V_R = V_S \tag{8}$$

$$nt_E = C_S V \tag{9}$$

Combination of equations (3), (5), (6) and (9) gives

$$t_E - t = [H^+]K_{HA}t + \frac{V}{n}([H^+] - [OH^-]) \times (1 + [H^+]K_{HA}). \tag{10}$$

When data from section A in Fig. 3 are evaluated, equation (10) can be approximated to:

$$t_E - t = \frac{V}{n}[H^+]. \tag{11}$$

In section B the mixed stream contains an excess of hydroxide ions and equation (10) can be approximated to:

$$t - t_E = \frac{V}{n}[OH^-] = \frac{V}{n}\frac{K_W}{[H^+]}. \tag{12}$$

If $[H^+]$ is measured potentiometrically, *e.g.*, with a glass electrode, the Nernst equation holds:

$$E = E^0 + S \log [H^+]. \tag{13}$$

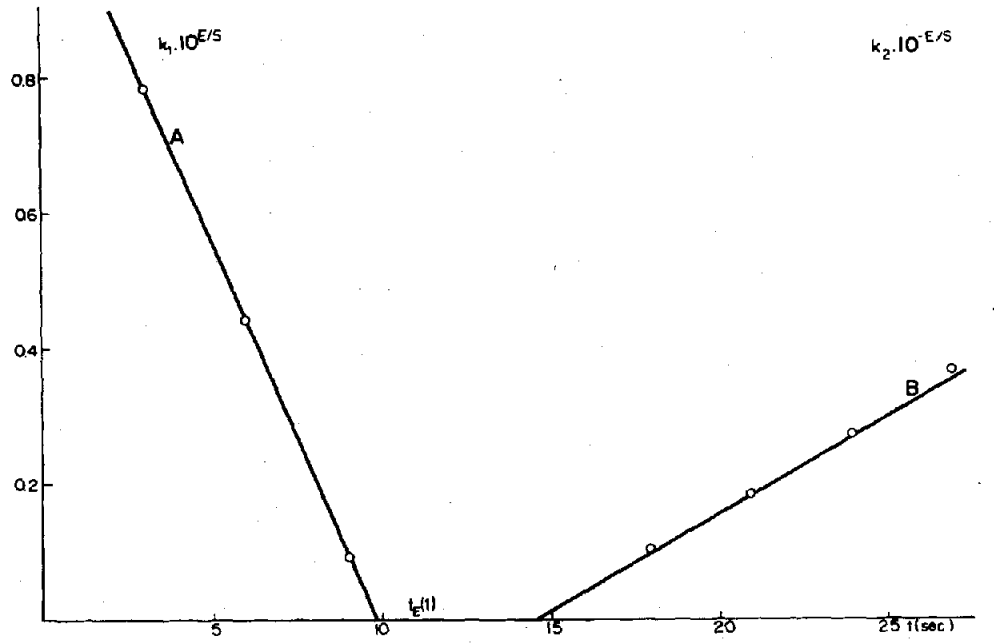

Fig. 5. Linear transformed titration curves obtained when data from Fig. 4 are evaluated by use of equation (11a) for branch A and (12a) for branch B.

If V and n are kept constant, equations (11) and (12) can be expressed as follows:

$$t_E - t = k_1 10^{E/S} \tag{11a}$$

$$t - t_E = k_2 10^{-E/S}. \tag{12a}$$

It is not necessary to know the absolute values of E^0, V, n and K_w because these parameters can be included in the constants k_1 and k_2 which can be arbitrarily chosen. The value of S should be known.

When equations (11a) and (12a) are plotted as functions of t, two straight lines are obtained. These lines theoretically intersect each other on the t-axis at the point t_E. Equation (11a) can be used for sections A and D in the determination of $t_E(1)$ and $t_E(2)$. Equation (12a) is used when data from branches B and C are evaluated for the determination of $t_E(1)$ and $t_E(2)$. This means that theoretically the equivalence points can be obtained automatically in an easy manner. When data from a real titration curve (Fig. 4) are evaluated by the method described, the curves given in Figs. 5 and 6 are obtained. However, as can

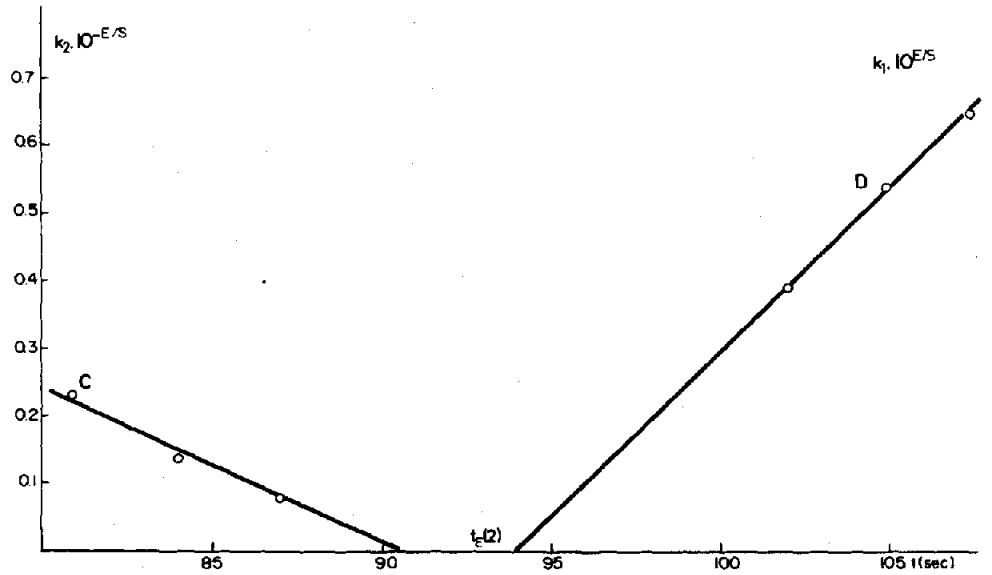

Fig. 6. Linear transformed titration curves obtained when data from Fig. 4 are evaluated with equation (11a) for branch D and (12a) for branch C.

be seen in these figures, neither branches A and B nor C and D intersect each other on the t-axis as in theory they should. The discrepancy is too great to be attributed to interference by carbonate in the flowing solution. The point of intersection of the two lines lies below the t-axis but coincides quite well with the point of the steepest part of the potential jumps in Fig. 4. The time interval corresponding to the distance between the two intersection points with the t-axis can be as much as 1–3% of the total program length (2τ). The smaller the 2τ-value and the lower the concentration of the acid, the longer this time interval. [For example, in titration of $10^{-4}M$ hydrochloric acid by a triangle program with a 95-sec length, the differences of $t_E(1)$ and $t_E(2)$ from the equivalence point were 2.5 and 1.5 sec, but were much shorter than 1% of the program length (95 sec) in the case of $10^{-3}M$ hydrochloric acid.]

The same is true for parts C and D of the titration curve in certain cases (low concentration, small 2τ-value). The branch D, although linear near the t-axis, is curved. This non-linearity is due to the tailing effect and is a drawback as it can make the automatic location of $t_E(2)$ quite difficult. The calibration graph of Q *vs.* concentration is linear.

When a weak acid, *e.g.*, acetic acid, is titrated a different transformation should be used for the linearization. Equation (10) can be approximated to

$$t_E - t = [H^+] K_{HA} t \tag{13}$$

or, if $[H^+]$ is measured potentiometrically:

$$t_E - t = k_3 10^{E/S} t \tag{13a}$$

When equation (13a) is used in the determination of t_E, the absolute starting point of the titration should be known. (In our case, however, t_0 is unknown.) This disadvantage can be overcome by the method for titration of weak acids given by Sørensen in his original paper.[13] Equation (13a) is divided by t and equation (13b) is obtained:

$$\frac{t_E}{t} - 1 = k_3 10^{E/S}. \tag{13b}$$

By plotting $10^{E/S}$ as a function of $1/t$ a straight line will be obtained. The line intercepts the $1/t$ axis at the point $1/t_E$. When t_E is determined in this way, t_0 can be arbitrarily chosen. Equation (13b) can be used to evaluate data from sections A and D. Equation (12a) should be used for sections B and C in the titration of weak acids. When data from a titration of $5 \times 10^{-4}M$ acetic acid Fig. 7 are evaluated by means of equations (13b) and (12a), the curves in Figs. 8 and 9 are obtained. Neither the branches A and B nor C and D give the same t_E. In construction of the calibration line the averages of the two $t_E(1)$ and $t_E(2)$ values are used. As can be seen in Fig. 8 the branch A is not linear but with increasing concentration of the acid, from about $8 \times 10^{-4}M$, the line will be straight. When equation (11a) is used in the evaluation of data from section A in the titration of acetic acid at concentrations less than $8 \times 10^{-4}M$, straight lines are obtained. At low concentrations acetic acid is dissociated to such a degree that the titration can be regarded as virtually a titration of a strong acid. Equation (12a) gives straight lines with data from sections B and C at any concentration. Data from section D give linear plots with equation (13b). Only at concentrations higher than $8 \times 10^{-4}M$ will the line near the equivalence point be curved.

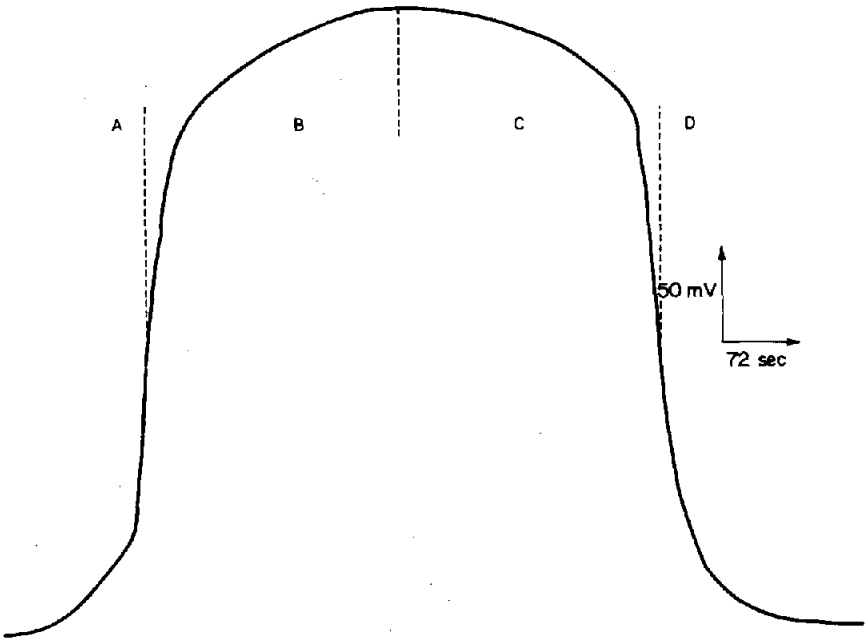

Fig. 7. Potentiometric triangle-programmed titration curve of $5 \times 10^{-4}M$ acetic acid, $i_{max} = 5$ mA; $2\tau = 130$ sec.

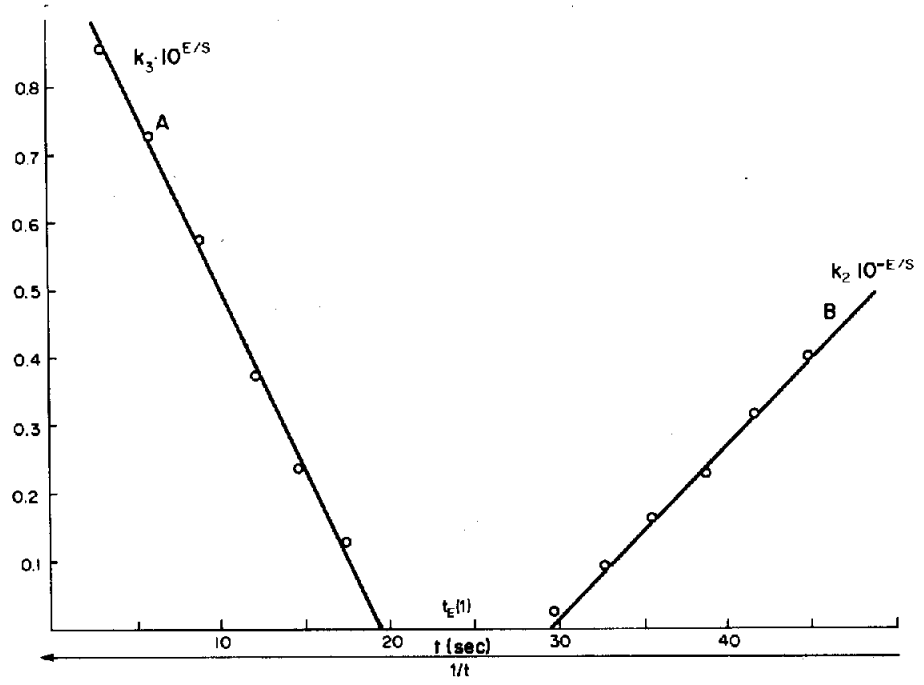

Fig. 8. Linear transformed titration curve obtained when data from Fig. 7 are evaluated with equation (13b) for branch A and (12a) for branch B.

Differentiation of the titration curve

Software method. The equivalence point of the titration can also be determined, as is well known, by differentiating the original $E = f(t)$ curve. The plot of dE/dt *vs.* t forms a peak with t_E at the top. When the second derivative d^2E/dt^2 is plotted as a function of t the curve obtained has two peaks, one on each side of the t-axis. The point where the plot crosses the t-axis between the peaks gives t_E. These methods are used only to locate the inflection point of the original titration curve. In most practical cases, the equivalence point and the inflection point are close enough for such techniques to be unnecessary. From the shape of the titration curves obtained in practice in our method, however, it is obvious that if an automatic software differentiation method is to be used, it must be combined with a curve-smoothing

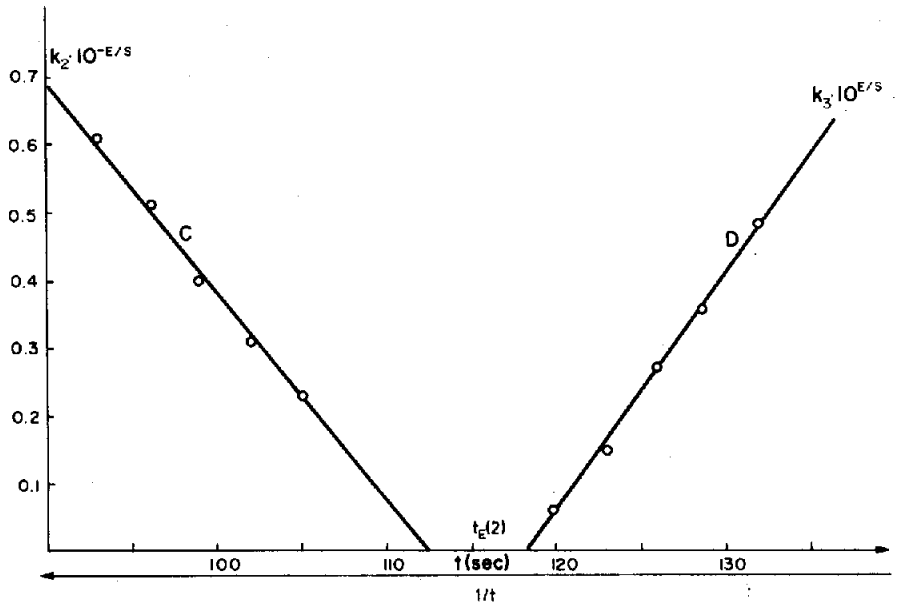

Fig. 9. Linear transformed titration curve obtained when data from Fig. 7 are evaluated with equation (13b) for branch D and (12a) for branch C.

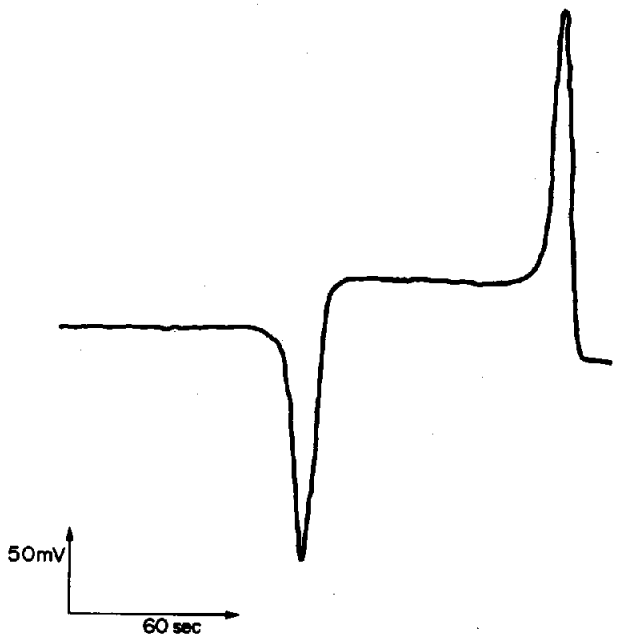

Fig. 10. The hardware differential curve of titration of $4 \times 10^{-4}M$ acetic acid, $i_{max} = 3.75$ mA, $2\tau = 144$ sec.

or curve-fitting procedure. In that way the effects of statistical and electrical noise can easily be eliminated. The curve smoothing or fitting, however, requires considerable off-line computer operation and a computer with considerable memory capacity. The detailed results of our studies of the computerized evaluation of triangle-programmed titrations with software differentiation will be published later.

Hardware method. A differential curve can also be obtained if two electrodes of the same kind are placed an appropriate distance apart in the direction of the flow.[9] By this method the concentration gradient between these two points is measured. The differential curve of the titration of acetic acid obtained by the hardware method is given in Fig. 10. The curve shows well-defined peaks at the two equivalence points. These peaks can easily be automatically located by digital or analogue methods.

Photometric methods

In the triangle-programmed photometric acid–base titrations an indicator is added to the solution to be analysed and the flow goes through a cell where the absorbance is measured. The most common method in batch titrations is to use an indicator which changes colour at the equivalence point. The colour change should be sharp and the measurement should be made at the wavelength of maximal difference between the absorbances of the acid and base forms of the indicator. All acid–base indicators which can be used in normal titrations are suitable.

A method, very attractive for automatic photometric determination of the equivalence point, is given by Mullen and Anton.[16] A mixture of Methyl Red and *m*-Cresol Purple (1.0 mg of each, dissolved in 100 ml of ethanol) is used in the titration of hydrochloric acid. Methyl Red changes from red to yellow over the pH range 4.4–6.2 and *m*-Cresol Purple from yellow to purple over the pH range 7.2–8.8. Between pH 6.2 and 7.2 a solution containing these two indicators is yellow. When a solution of a strong acid is titrated and these two indicators are used, at the equivalence point, there is sharp peak in the absorbance. Before the titration 1 ml of indicator is added to 10 ml of sample (or standard). The experimental curve of such a titration of hydrochloric acid is given in Fig. 11. Peaks are obtained at the two equivalence points $t_E(1)$ and $t_E(2)$. It is obvious that the peaks can conveniently be located automatically. The calibration curve is linear.

Linear transformation of the photometric titration curve

If a single-colour indicator is used for the titration, the evaluation must be based on an appropriate transformation of the titration curve. For example the photometric titration curve can be transformed into a linear plot.[17–19] When the absorbance of the flow-stream is measured, $[H^+]$ can be calculated from the following equation, the usual assumptions being made:

$$[H^+] = \frac{A_{In} - A}{(A - A_{HIn})K_{HIn}} \qquad (14)$$

where K_{HIn} is the stability constant of the indicator, A is the absorbance of the solution, A_{HIn} and A_{In} are the absorbances when the indicator is completely in its acid and base form respectively. For the titration

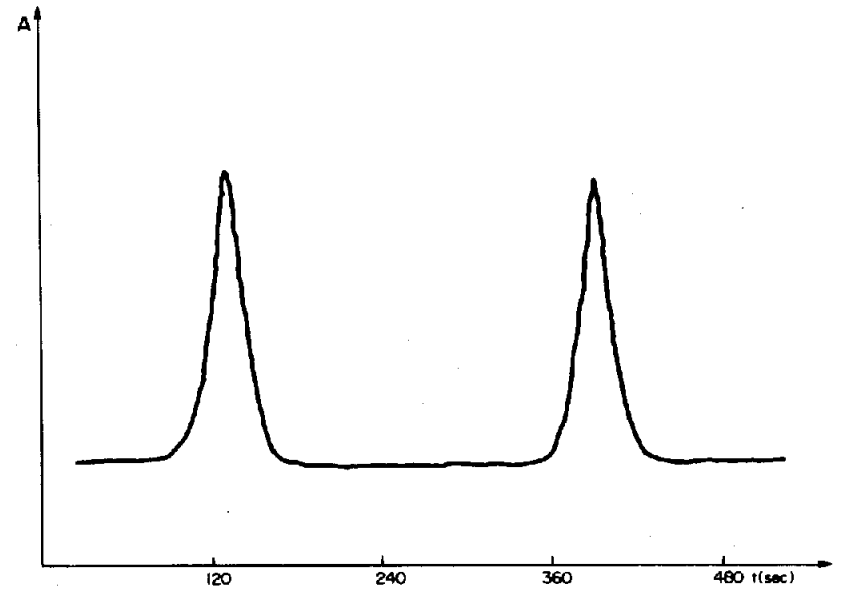

Fig. 11. Triangle-programmed photometric titration curve of 5×10^{-4} *M* hydrochloric acid. A mixture of Methyl Red and *m*-Cresol Purple is used as indicator, $i_{max} = 9.4$ mA; $2\tau = 330$ sec; $\lambda = 565$ nm.

of a strong acid equation (15) is valid:

$$t_E - t = k_4 \frac{A_{In} - A}{A - A_{HIn}} \qquad (15)$$

and when weak acids are titrated, equation (16) can be used:

$$\frac{t_E}{t} - 1 = k_5 \frac{A_{In} - A}{A - A_{HIn}}. \qquad (16)$$

In both cases the indicator should be chosen so that the colour change appears somewhere near the half-titration point. Equations (15) and (16) are valid when parameters n and V are constant. In the titration of a strong acid Quinaldine Red can be used as indicator.[19] Bromocresol Green[19] and *p*-ethoxychrysoidine can be used when acetic acid and other weak acids of similar strength are titrated. In the triangle-programmed titration technique where the equivalence point is passed twice an indicator changing its colour in the alkaline pH region can also be chosen. Phenolphthalein changes its colour in the pH-range

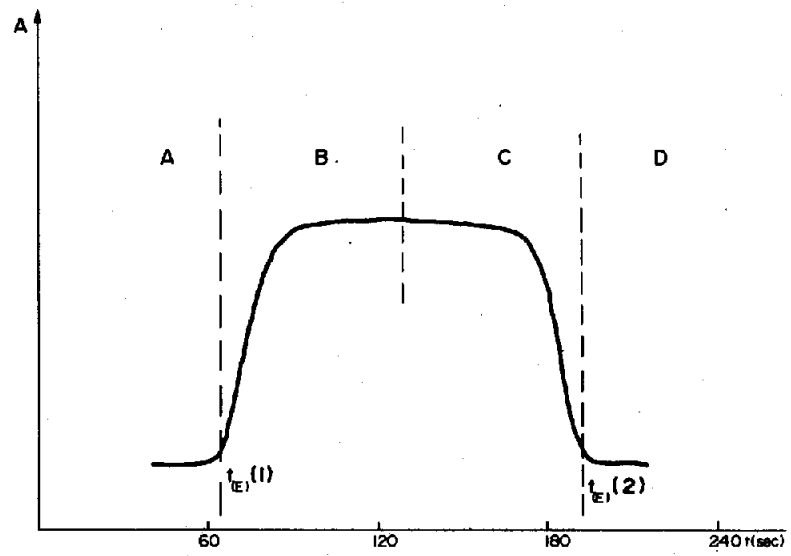

Fig. 12. Triangle programmed photometric titration curve for acetic acid. Phenolphthalein as indicator, $\lambda = 550$ nm; $i_{max} = 9.4$ mA; $2\tau = 120$ sec.

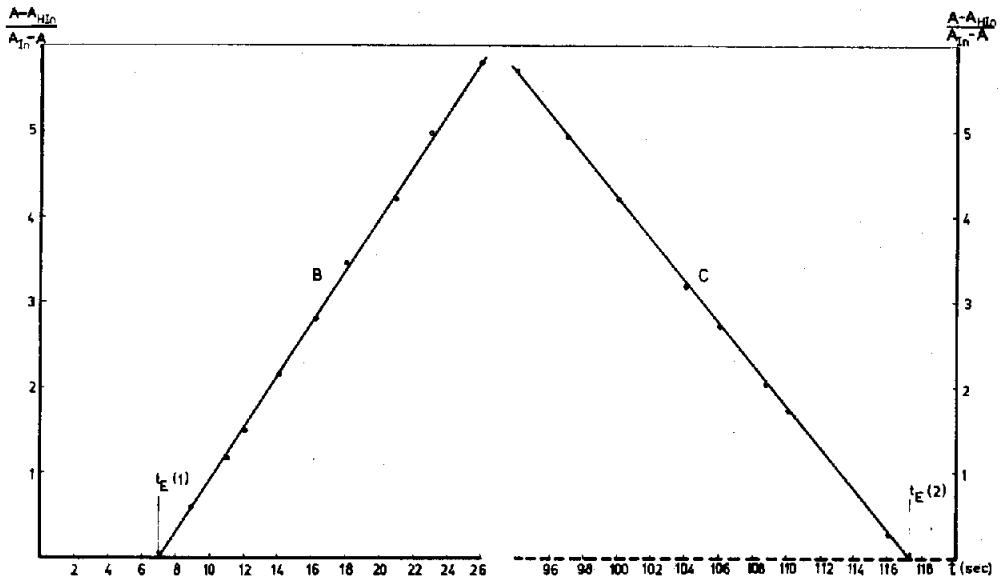

Fig. 13. Linear titration curves obtained when data from Fig. 12 are evaluated with equation (17).

8–10 and can thus be used to determine the equivalence points $t_E(1)$ and $t_E(2)$ from points in sections B and C respectively. Equation (17) should then be used.

$$t - t_E = k_6 \frac{A - A_{HIn}}{A_{In} - A} \qquad (17)$$

A titration curve for $7 \times 10^{-4} M$ acetic acid, obtained with phenolphthalein as indicator is given in Fig. 12. Two of the transformation graphs are shown in Fig. 13. The calibration graph is linear.

DISCUSSION

It is obvious from the results shown, that both potentiometric and photometric methods can be used as detection techniques in triangle-programmed titrations.

The evaluation of the titrations basically relies on accurate location of the two equivalence points, and measurement of the value Q. A calibration curve or calculation then gives the unknown concentration. Various equivalence-point location methods have been investigated. Each has its own advantages and drawbacks. The most serious source of error in the potentiometric methods is the electrical noise, which can sometimes result in failure of the whole method. These errors are avoided in the photometric method, but the choice of a suitable indicator may be difficult. The indicator may also react with the ions generated. This indicator error can be avoided by having the same concentration of indicator both in the standard solution and in the analyte. When the method of linear transformation of the photometric titration curve is used, *i.e.*, equations (15) and (16), the concentration of the indicator should be less than 1% of the concentration of the acid. Equations (15) and (16) have been derived by assuming that only one acid reacts with the hydroxide ions generated. If the concentration of the indicator is too high its reaction with the hydroxide ions cannot be neglected and the solution contains two acids which react with the hydroxide ions. Equations (15) and (16) are then no longer valid, and the lines will not be straight either. The indicator is also often adsorbed on the walls of the tubes and the cell, causing problems when the indicator is changed. In the photometric methods the problems of electrical coupling between the generating and indicating circuits are avoided.

The determination of the equivalence point by the method of linearized plots seems not very attractive in the triangle-programmed titration method. Titration data both before and after the equivalence point are needed in the calculations and different equations should be used for the evaluation of data from different sections of the curve. In the potentiometric methods the tailing effect can also cause some difficulties in the automatic evaluation of data from section D in titration of strong acid, as can be seen in Fig. 6. In titration of weak acids the branch A is slightly curved as can be seen in Fig. 8 and the linearity of the curve also depends on the concentration of the acid and makes the determination of $t_E(1)$ difficult. Sometimes the calibration curve for weak acids is not linear at low concentrations. When the method of linear plots is used in the photometric method the absorbance values A_{In} and A_{HIn} are needed. A_{In} can easily be determined because it is the same as the absorbance of the flow between the two equivalence points. The value of A_{HIn} can be calculated as the average of the absorbance values before and after the titration program. The method of linear plots needs a data collection and storage device and a small computer to perform the calculations.

In the potentiometric method, hardware differentiation seems to be the most advantageous method. It is independent of the character of the acids to be titrated and can be used for both strong and weak acids. Only the appearance of the potential peaks must be determined, which can easily be done automatically. If the acid is very weak a proper potential jump is not obtained and the method cannot be used.

In the photometric method the use of two indicators gives quite an easy and reliable method in the determination of the equivalence points in titration of strong acids. The restriction of the method is perhaps the lack of suitable indicators for the titration of weak acids.

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THE EFFECT OF TRACE LEVELS OF CYANIDE ON THE FORMATION OF MERCURY–IODIDE COMPLEXES

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Summary—The interference of trace levels of cyanide with the formation of iodo-mercury complexes is made the basis of a method of trace analysis for cyanide. The decrease in absorbance of the iodo-mercury complexes is a linear function of total cyanide concentration up to about $5 \times 10^{-5}M$ in $0.1M$ sodium hydroxide medium when the iodide and mercury total concentrations are $0.05M$ and $3 \times 10^{-5}M$ respectively. Several cyano-mercury complexes are formed simultaneously, and quite a large fraction of the cyanide remains uncomplexed.

Mercury(II) with excess of iodide solution forms the highly stable complexes HgI_2, HgI_3^- and HgI_4^{2-}, the last being the predominant species if the iodide concentration is high enough (*e.g.*, $> \sim 0.01M$). The measurement of the absorbance at 323 nm of the mercuric tetraiodide complex in $1M$ iodide solution has been used for the estimation of ppm concentrations of mercury(II).[1] Cyanide interferes by formation of complex species of the type $Hg(CN)_n^{(n-2)-}$ and mixed-ligand species $Hg(CN)_nI_{(4-n)}$ in neutral media. Penneman and Jones[2] have demonstrated the existence of these complexes by infrared studies. The interference of cyanide is exploited in the method described here (and also by Clyde and Warner[3] in a recent paper†).

The work described here was carried out to identify the conditions favouring the interference of trace levels of cyanide, and to utilize the interference for estimation of trace cyanide.

THEORY

If, in view of the relevant stability constants, we neglect the formation of hydroxo-complexes in presence of excess of iodide, the general reaction between mercury(II) and iodide may be represented by

$$Hg^{2+} + xI^- \rightleftharpoons HgI_x^{(x-2)-} \qquad (1)$$

The overall equilibrium constants for this reaction are given by

$$\beta_x^I = \frac{[HgI_x^{(x-2)-}]}{[Hg^{2+}][I^-]^x} \qquad (2)$$

Mercury(II) also reacts with cyanide:

$$Hg^{2+} + nCN^- \rightleftharpoons Hg(CN)_n^{(n-2)-} \qquad (3)$$

$$\beta_n^{CN} = \frac{[Hg(CN)_n^{(n-2)-}]}{[Hg^{2+}][CN^-]^n}. \qquad (4)$$

The decrease in absorbance, ΔA, of any of the iodo-complexes, will be a function of the iodide, mercury and cyanide concentrations since the first two of these will govern the distribution of iodo-species, and the last two the distribution of cyano-species.

Complications may be caused by the formation of mixed-ligand complexes such as iodo-hydroxo complexes, but in general the effect on the calculated distribution of the mercury species will be comparable with that caused by the uncertainties in the published stability constants for the complexes.

From equations (2) and (4) it is evident that if the iodide concentration is very much greater than that of the mercury and cyanide the change in iodide concentration caused by competitive cyanide complex formation will have practically no effect on the distribution of the mercury iodide complexes. Hence the effect of cyanide can be monitored by measuring the change in concentration of any of the iodo-complexes. Clyde and Warner used the HgI_4^{2-} species, measuring the decrease in its absorbance at 323 nm.

The relationship between this decrease in absorbance and the total cyanide concentration will be a complex function of various factors, but for fixed total iodide and mercury concentrations and a fixed pH will be determined by the stability constants for the cyanomercurate complexes. It follows from the closeness of β_2, β_3 and β_4 for these complexes‡ that all three will be present simultaneously, but $Hg(CN)_2$ will predominate so long as $[CN^-] < \beta_2/\beta_3$, *i.e.*, $< 10^{-4}M$, and $Hg(CN)_4^{2-}$ will not predominate until $[CN^-] > \beta_3/\beta_4$, *i.e.*, $> 10^{-3}M$. Since $[CN^-]$ is here the *free* cyanide concentration, then if the total cyanide is $< 10^{-4}M$, the major species will certainly

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† The present work was in fact completed in 1976, and the delay in publication is due entirely to the insistence of the referee and Editor-in-Chief that the theory be explored as thoroughly as possible [Ed.].

‡ $\log \beta_2 = 34.5$, $\log \beta_3 = 38.5$, $\log \beta_4 = 41.6$.

be $Hg(CN)_2$. However, as the cyanide concentration increases, the relative proportions of the higher cyanide complexes will also increase. It follows that the relationship between cyanide concentration and decrease in absorbance will not be a linear function of the cyanide concentration, though it may approximate to one over a certain concentration range.

The work described here was therefore a systematic investigation of the effect of varying the conditions, with a view to finding the optimum set.

EXPERIMENTAL

Reagents

Analytical grade chemicals were used where possible.

Mercury(II) stock solutions, $5 \times 10^{-3}M$ (1000 ppm). Mercuric oxide (1.08 g) and potassium iodide (16.6 g) dissolved in distilled water and diluted to 1 litre or mercuric chloride (1.355 g) dissolved in distilled water and made up to 1 litre.

Potassium iodide solution, 1.0M.

Cyanide stock solution, $3.85 \times 10^{-3}M$ (1000 ppm). Potassium cyanide (2.50 g) dissolved in 100 ml of 1.0*M* sodium hydroxide and diluted to 1 litre; standardized weekly by titration with 0.05*M* silver nitrate.[4]

All working solutions, made from the stock solutions by suitable dilution and mixing, were 0.1*M* in sodium hydroxide unless otherwise stated.

Procedure

Solutions of the required composition were prepared by suitable dilution and mixing of the stock solutions, and the absorbances were measured at the appropriate wavelengths.

The maximum total concentrations employed were: cyanide $6.2 \times 10^{-5}M$; mercury(II) $5 \times 10^{-5}M$; iodide 0.1*M*; sodium hydroxide 0.1*M*. Hence, the ionic strength of the reaction medium never exceeded 0.2 (but was mostly less than 0.15), and all the free cyanide was in ionic form as CN^-.

DISCUSSION OF RESULTS

Iodo-mercury complexes

Provided the free iodide concentration in the sample solution, $[I^-]_s$ is practically the same as that in the reference, $[I^-]_r$, two peaks are obtained in the spectrum (Fig. 1), the peaks shifting towards shorter wavelengths with decreasing iodide concentration, especially the peak at ~270 nm. In this work the reference solutions were therefore always matched in iodide concentration with the test solutions.

Both peaks must be assigned to the HgI_4^{2-} complex, because the molar absorptivity would be of the order of 10^7 l.mole^{-1}.cm^{-1}, *i.e.*, about 100 times the commonly accepted theoretical maximum, if the sole absorbing species were HgI_3^- (see below for equilibrium concentrations of the species). The shift in wavelength with decrease in iodide concentration may indicate that HgI_3^- absorbs in the same regions as HgI_4^{2-}, since lower iodide concentration favours formation of HgI_3^- (the two species should be in equi-

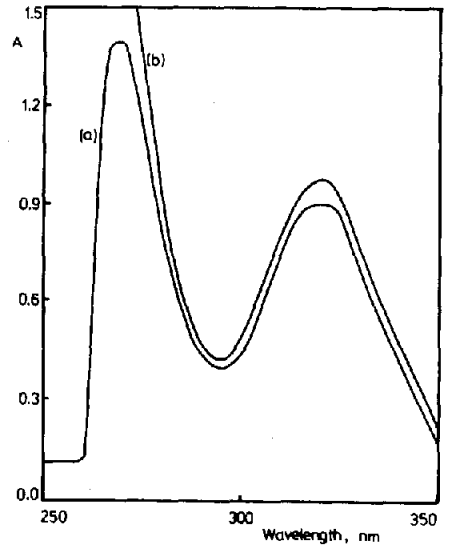

Fig. 1. Spectra of iodo-mercury complexes in 0.1*M* potassium iodide medium, measured against (a) 0.1*M* potassium iodide and (b) water.

molar ratio when $[I^-] = \beta_3/\beta_4 = 10^{26}/10^{30} = 10^{-4}M$).* The apparent molar absorptivity also changes with iodide concentration (Fig. 2); this and the wavelength shift could be due to a structural change in the solvent or to an ionic strength effect and the change in the distribution of the complexes.

Cyanide interferences

The cyanide interference, as measured in terms of reduction ΔA in the absorbance of the mercury iodide complexes, increases with decreasing iodide concentration as expected from the theory (Fig. 3). A limiting factor in obtaining higher ΔA values with a fixed amount of cyanide is that the absorbance of the mercury iodide complexes decreases sharply as the iodide concentration falls below 0.1*M*. The iodide concentration range where maximum absorbance readings A_0 may be obtained in the absence of cyanide, together with large absorbance depressions ΔA in the presence of cyanide, is 0.02–0.1*M*. For this reason the cyanide interference was studied largely in the iodide concentration range 0.005–0.1*M*. Both peaks behave alike towards cyanide interference; the sharper peak (at 265–278 nm) was used to study the effects of cyanide.

Cyanide interference is greatly enhanced in strongly basic conditions. For example, no absorbance depression is observed in neutral or $10^{-4}M$ hydroxide medium until the cyanide–mercury molar ratios are above 2.0 and 1.0, respectively. On the other hand, with alkali concentrations above $10^{-2}M$ in the medium, there is depression of the absorbance with cyanide–mercury mole ratios from 0.2 to 2.0. The best ΔA values are obtained in 0.05–0.1*M* hydroxide medium. Cyanide interference in such basic media is essentially linear in effect up to a cyanide–mercury mole ratio of about 2 (Fig. 4), except when the iodide

*The stability constants quoted in the literature vary considerably. The values used here have been rounded off and are used mainly for illustrative purposes.

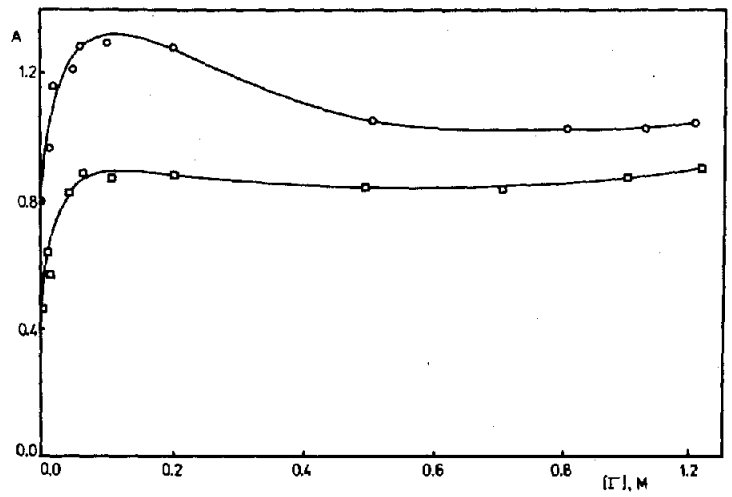

Fig. 2. Absorbance of iodo-mercury complex, as a function of iodide concentration, measured at (a) 268–273 nm and (b) 323 nm.

concentration is below about 0.03*M*. The slopes of plots of ΔA (or A) against cyanide concentration increase only slightly with decreasing iodide concentration.

Clyde and Warner[3] stated that the absorbance decreased at pH 11 and attributed this to abstraction of mercury(II) from the iodo-complex by the hydroxide. As they do not specify *which* absorbance decreases, the statement is not very helpful, but as the ratio $[HgI_4^{2-}]/[Hg(OH)_2]$ should be equal to $\beta_{HgI_4}[I^-]^4/\beta_{Hg(OH)_2}[OH^-]^2 \sim 10^{30}/(10^{22} \times 10^{-6}) \sim 10^{14}$ for $[I^-] = 1.0M$ and pH 11 (the conditions used by Clyde and Warner), this explanation seems improbable. Figure 4 shows that even at pH 13, with 0.05*M* iodide, the mixed-ligand species $Hg(CN)_2OH$ is only a minor component of the system; the ratio of $[HgI_4^{2-}]/[Hg(OH)_2]$ under these conditions should still be of the order of 10^5, so it seems likely that they mean that the absorbance decreases more at pH 11 in the presence of cyanide, which could be explained by the fact that the cyanide should be almost completely in the ionic form at this pH. These authors also stated that varying the pH between 5 and 9 had no effect, but again they do not make it clear whether the pH refers to that of the sample being tested or the final solution. The fact that they obtained a linear calibration curve for $[CN^-]_{total}/[Hg^{2+}]_{total}$ ratios ranging up to 10:1, when compared with the findings in the present paper, seems to indicate that the cyanide was in fact protonated to some extent. From $pK = 9.2$ for

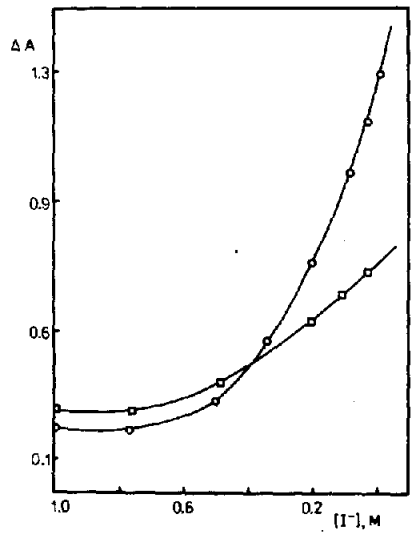

Fig 3. Absorbance depression ΔA as a function of iodide concentration ($5 \times 10^{-5}M$ Hg, 1.94×10^{-4} CN^-), measured at (a) 268 nm and (b) 323 nm.

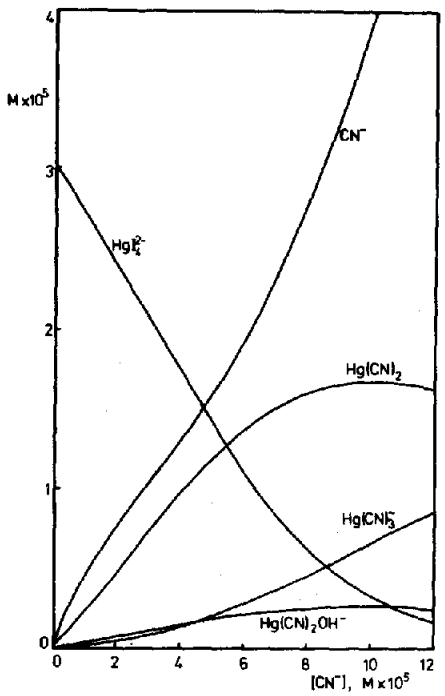

Fig. 4. Distribution of various species as a function of total cyanide concentration ($3 \times 10^{-5}M$ Hg, 0.05*M* I^-, 0.1*M* OH^-).

HCN, it would be expected that at pH 9 just over half the uncomplexed cyanide would be in protonated form and at pH 7 over 99% would be present as HCN. This may also help to account for their observation that if the mercury concentration was doubled from $2.0 \times 10^{-4}M$ to $4 \times 10^{-4}M$ there was a profound effect on the absorbance decrease on addition of cyanide, but again there is a lack of clarity in their paper. The caption to their Fig. 1 does not say whether these values refer to the total mercury concentration in the solution measured, or the concentration of the reagent added. If the latter is the case, it is difficult to see how use of $5 \times 10^{-4}M$ mercury(II) reagent (as in the procedure) could work; if the former, the lower concentration used is already ten times that used in the procedure, and increasing it may simply result in a decreased slope for the calibration curve. From the absorbances and molar absorptivity quoted it can be deduced that the concentrations refer to the reagent. A simplified calculation based on the assumption that HgI_4^{2-} and $Hg(CN)_2$ are the only complexes formed shows that under Clyde and Warner's conditions the ratio $[HgI_4^{2-}]/[Hg(CN)_2] = \beta_{HgI_4}[I^-]^4/\beta_{Hg(CN)_2}[CN^-]^2$ exceeds 1 when $[CN^-] < 10^{-2.25}$, and 100 when $[CN^-] < 10^{-3.25}$. Clyde and Warner's Fig. 1 indicates that with the $4.0 \times 10^{-4}M$ reagent there is no formation of cyanide complexes until the cyanide concentration is at least $2.1 \times 10^{-4}M$ (or $[CN^-] > 10^{-3.7}M$), in agreement with this.

The values of n for $Hg(CN)_n$ (which range between 2.0 and 2.2) calculated from the slopes of plots of log ΔA *vs.* log $[CN]_{total}$ on the simplifying assumption that only one complex is formed, indicate that the major cyanomercurate complex in 0.03–0.06M iodide medium is $Hg(CN)_2$.

A HALTAFALL calculation of the distribution of the various species in the solution (Table 1) confirms this observation for the conditions finally selected for the determination: $Hg(CN)_2$ is formed predominantly, especially at the lower concentrations of cyanide. $Hg(CN)_4^{2-}$ is the cyanide complex with the lowest concentration. The species next in importance to $Hg(CN)_2$ is $Hg(CN)_3^-$. The ratio $[Hg(CN)_3^-]$: $[Hg(CN)_2]$ increases with increasing cyanide concentration, and $[Hg(CN)_2]$ passes through a maximum. It is interesting that a large fraction of the cyanide remains uncomplexed. The contribution of the mixed-ligand species $Hg(CN)_2OH^-$ is comparatively small. Most importantly, however, the concentration of HgI_4^{2-} decreases linearly as the cyanide concentration increases up to about $6 \times 10^{-5}M$.

It is this last feature that is the basis for the measurement of trace quantities of cyanide. Advan-

Table 1. HALTAFALL calculation of equilibrium concentrations for $3 \times 10^{-5}M$ Hg, $0.05M$ I^-, $0–12 \times 10^{-5}M$ CN^- (total concentrations) in $0.1M$ NaOH medium

Total $[CN^-]$, $10^{-5}M$	$\log[HgI_2]$	$\log[HgI_3^-]$	$\log[HgI_4^{2-}]$	$\log[CN^-]$	Constants used
0	−7.720	−6.922	−4.525	—	
1	−7.759	−6.961	−4.564	−5.316	
2	−7.817	−7.019	−4.621	−5.107	
3	−7.884	−7.086	−4.689	−4.978	$\log\beta_{Hg(CN)_2} = 34$
4	−7.962	−7.163	−4.766	−4.877	$\log\beta_{Hg(CN)_3} = 38$
5	−8.050	−7.252	−4.854	−4.789	$\log\beta_{Hg(CN)_4} = 41$
6	−8.151	−7.352	−4.955	−4.707	$\log\beta_{HgI_2} = 24$
7	−8.265	−7.466	−5.069	−4.628	$\log\beta_{HgI_3} = 26$
8	−8.391	−7.593	−5.195	−4.551	$\log\beta_{HgI_4} = 30$
9	−8.528	−7.729	−5.331	−4.476	$\log\beta_{Hg(CN)OH} = 14$
10	−8.670	−7.871	−5.473	−4.403	$\log\beta_{Hg(CN)_2OH} = 20$
11	−8.812	−8.013	−5.616	−4.334	
12	−8.951	−8.152	−5.754	−4.270	

Total $[CN^-]$, $10^{-5}M$	$\log[Hg(CN)_2]$	$\log[Hg(CN)_3^-]$	$\log[Hg(CN)_4^{2-}]$	$\log[Hg(CN)OH]$	$\log[Hg(CN)_2OH^-]$
0	—	—	—	—	—
1	−5.687	−7.003	−9.219	−6.971	−6.487
2	−5.327	−6.434	−8.441	−6.820	−6.127
3	−5.136	−6.113	−7.991	−6.758	−5.936
4	−5.012	−5.888	−7.665	−6.735	−5.811
5	−4.924	−5.713	−7.401	−6.736	−5.724
6	−4.862	−5.569	−7.176	−6.755	−5.662
7	−4.819	−5.447	−6.975	−6.790	−5.619
8	−4.791	−5.342	−6.793	−6.840	−5.591
9	−4.777	−5.253	−6.628	−6.901	−5.577
10	−4.773	−5.176	−6.479	−6.970	−5.573
11	−4.778	−5.112	−6.346	−7.044	−5.578
12	−4.789	−5.059	−6.229	−7.119	−5.589

tage is taken of the relation between ΔA and the cyanide concentration, and the relatively large slopes of the plots, allowing the determination of cyanide concentrations as low as 0.1 μg/ml in suitably alkaline iodide solution.

Determination of cyanide

From a burette add 25-ml aliquots of a solution 0.1*M* in potassium iodide, $6 \times 10^{-5}M$ in mercury(II) and 0.1*M* in sodium hydroxide, to ten 50-ml standard flasks. In eight of the flasks place various volumes from 0 to 14 ml of 5-ppm cyanide solution in 0.1*M* sodium hydroxide. To the other two flasks add different volumes of the unknown cyanide solution, made 0.1*M* in sodium hydroxide. Make all the solutions up to the mark with 0.1*M* sodium hydroxide and mix them. Read the absorbances at 268 nm, against 0.05*M* potassium iodide in 0.1*M* sodium hydroxide. Read the cyanide contents of the sample from a calibration curve of A (or ΔA) *vs.* cyanide concentration in ppm or mole/l.

The only disadvantage is the interference from other heavy metals. This is common with most methods of cyanide analysis. On the other hand, the technique is very fast compared with other chemical methods; it is reasonably sensitive, and the interference which is usually observed in neutral solutions from traces of organic compounds such as aldehydes, methanol and acids, is eliminated by use of the alkaline medium.

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SHORT COMMUNICATIONS

ANALYTICAL BEHAVIOUR OF POLY(VINYL ACETATE) AND ITS HYDROLYSIS PRODUCTS WITH IODINE

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Summary—Formation of the red complex between poly(vinyl acetate) and iodine in the presence of iodide is quantitatively independent of the method by which the polymer is prepared. In contrast, the amount of complex formed in the case of partly hydrolysed products of poly(vinyl acetate) depends strongly on the source of this polymer and may vary from sample to sample by as much as a factor of five, while the use of different hydrolysis methods gives rise to even greater differences in the amount of complex formed by the products. The determination of partly hydrolysed poly(vinyl acetate) through the red iodine complex is recommended only when the standard polymer sample and the unknown have been prepared in the same batch. Details of these systems are discussed.

Complexation of poly(vinyl acetate) (PVAc) with iodine in the presence of iodide has been demonstrated as a method for the determination of this polymer.[1] In a development of the method, the absorbance of the red complex at 510 nm (A) yielded accurately linear calibration curves, $A = 0.022c$, for the concentration range c = 25–100 mg of polymer per litre of final solution in the case of two polymers of different molecular weight obtained from the same source.[2] Certain partly hydrolysed products of PVAc also form a red complex,[3–7] but no systematic investigation has been reported, as far as we are aware, of the suitability of this complex as the basis of an analytical method. Moreover, the quantity of red complex formed by certain partly hydrolysed products appears to depend on the method of hydrolysis used,[8–14] as this may influence the length and frequency of the block sequences of acetate and alcohol groups along the polymer molecular chains.[7,15] We have felt the need, therefore, first to test pure PVAc samples obtained from all common sources to establish whether or not the sensitivity of red complex formation can vary at all with the source of the polymer. Then the same polymers have been hydrolysed to an extent within the range of commercial interest and the sensitivity of the partly hydrolysed products for red complex formation has been determined to assess the analytical potential of the procedure for these products.

EXPERIMENTAL

PVAc samples were obtained from all the known commercial sources, and three specimens were prepared in the laboratory (Table 1). The degree of hydrolysis of the products resulting from hydrolysis[7] of the PVAc samples was determined as previously described[7,16] (Table 2). Methanol was of reagent grade, and other reagents were of analytical grade unless otherwise stated. The procedures used are given below. Details of preliminary exploration are omitted.

The pure PVAc samples were each tested as follows.[1,2] In each of ten 10-ml standard flasks were placed 5 ml of 0.0212M methanolic iodine solution. Suitable aliquots of 0.03035M methanolic PVAc solution were added (molarity based on the vinyl acetate segment of molecular weight 86.09), and the volume was made up to 10 ml with methanol (a blank containing no polymer was also prepared). One ml of each of these solutions was diluted to 25 ml with 0.0169M aqueous potassium iodide with very gentle swirling to avoid partially precipitating the colloidal red complex. After 1 hr, the spectra of the solutions, which had a poly(vinyl acetate) concentration up to 0.000486M, were measured in 1-cm cells at 20 ± 0.2° with a Unicam SP500 or SP700 spectrophotometer, with the blank solution in the reference beam.

The Aldrich PVAc sample was hydrolysed by three distinct methods[7] to within the range 91 ± 1 mole% of hydroxyl groups, and accurately linear calibration curves were established for iodine complex formation in test solutions of the products as follows. Ten solutions were made up in 50-ml standard flasks from suitable aliquots of aqueous polymer solution (80–90% hydrolysed PVAc does not dissolve in methanol) diluted to 20 ml with distilled water and mixed with aqueous iodine/iodide solution and water to give final total concentrations of 0.0002M iodine and 0.0054M iodide. The ranges of polymer concentration were varied in proportion to their sensitivity to iodine complex formation. Spectra were scanned as before, and absorbances per concentration unit (mg/l.) at λ_{max} are recorded in Table 2.

Nine of the pure PVAc samples were reliably hydrolysed by methoxide-catalysed trans-esterification in methanol[7] to within the range 81 ± 1 mol%, and test solutions of the products were compared as follows. Fifty ml of solution were made up in standard flasks as above, to give final total concentrations of 0.0015M iodine, 0.0045M iodide and 0.01M polymer. Results are in Table 2.

Table 1. Absorption coefficients for iodine complexes formed at 20°C by poly(vinyl acetate) from various sources, with 0.000423*M* iodine and 0.0162*M* potassium iodide in 4% methanol–water mixture

Source of polymer	Molecular weight*	Absorption coefficient†
Hopkin & Williams	33×10^3	2.45
BDH	45×10^3	2.18
Koch-Light	45×10^3	2.24
Aldrich	70×10^3	2.28
Solution polymerization‡	70×10^3	2.43
BDH	160×10^3	2.28
K & K	160×10^3	2.25
UV radiation‡	160×10^3	2.32
Fisons	260×10^3	2.23
Suspension polymerization‡	1050×10^3	2.13
Monsanto§	500×10^3	2.2 (ref. 2)

* Approximate viscosity average.
† For λ_{max} 520 nm; $10^2 \times$ absorbance/polymer concentration (in mg/l.).
‡ Polymer prepared in the laboratory.
§ Gelva V7 and V100 polymers.[2]

Table 2. Absorption coefficients for iodine complexes formed at 20°C by partly hydrolysed poly(vinyl acetate) polymers with iodide and potassium iodide in water

Source of PVAc	Method of hydrolysis	λ_{max}, *nm*	Absorption coefficient*
(*a*) *Results for* 81 *mol*% *hydrolysed PVAc*†			
Aldrich	Trans-esterification	490	0.22
Hopkin & Williams	Trans-esterification	490	0.18
UV radiation	Trans-esterification	500	0.16
K & K	Trans-esterification	500	0.14
Koch-Light	Trans-esterification	490	0.14
BDH 160000	Trans-esterification	495	0.14
Suspension polymerization	Trans-esterification	495	0.11
BDH 45000	Trans-esterification	500	0.06
Solution polymerization	Trans-esterification	510	0.05
(*b*) *Results for* 91 *mol*% *hydrolysed PVAc*‡			
Aldrich	Saponification	485	0.13
Aldrich	Trans-esterification	485	0.05
Aldrich	Acid equilibration	485	0.0015

* Defined as in Table 1.
† With 0.0015*M* iodine and 0.0045*M* potassium iodide.
‡ With 0.0002*M* iodine and 0.0054*M* potassium iodide.

RESULTS AND DISCUSSION

The absorption coefficients shown in Table 1 for complex formation by the ten pure PVAc samples studied have the mean value 2.28 and standard deviation 0.10 (confirming the generality of the result previously recorded[2]). However, there is probably a tendency for increases in molecular weight (MW) to cause a slight decrease in the coefficients. Nevertheless, the general agreement between the results establishes that with a calibration curve prepared with any pure PVAc polymer as standard, the reported method may be applied to the determination of an unknown sample of PVAc with an expectation of an error of not more than 10%.

The absorption coefficients shown in Table 2 for the hydrolysed PVAc products, on the other hand, show wide discrepancies. We are surprised that the coefficients in group (*a*) are spread by a factor as great as five, because we have been at pains to carry out the hydrolysis as uniformly as possible, and this suggests that the method of preparation of the PVAc from its monomer may in some way influence the structure of the hydrolysed products and their ability to complex with iodine. There is a rough correlation between the absorption coefficient and λ_{max} but not between the coefficient and MW. When different hydrolytic methods are deliberately used, as for group (*b*), and other variables in the system are kept uniform, the range of absorption coefficients is even greater. Whilst the individual results were generally reproducible (within $\pm 2\%$)[2] and satisfactory linear relationships between absorbance and concentration of polymer were observed, it is clear that the use of the red iodine complex for the determination of hydrolysed PVAc polymers must be subject to gross

errors unless a pure sample of the particular polymer to be determined can be used as a standard.

The results in Table 1 and Table 2(*a*) were obtained with the use of iodine and iodide concentrations sufficient to ensure complete formation of the complex.[1,2] Thus, when the iodide and iodine concentrations were reduced by a factor of 4, the absorption coefficients in Table 1 were reduced by only *ca.* 10%. The coefficients for the hydrolysed polymers were slightly sensitive to iodide concentration, the optimum value of this being *ca.* 0.005*M*. Addition of 0.05*M* sodium chloride to the test solutions had no appreciable effect. In order to verify a Beer's law relationship for the polymer hydrolysed by acid equilibration, Table 2(*b*), a lower iodine concentration was used so that the broad maximum of the complex centred at 485 nm should not be swamped by the wing of the intense iodine absorption band with $\lambda_{max} \sim 460$ nm.[3]

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A SENSITIVE COLORIMETRIC METHOD FOR ESTIMATION OF ASCORBIC ACID

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Summary—The reaction of ascorbic acid with ammonium molybdate to give molybdenum blue was investigated and used for microestimation of the vitamin in the pure state, dosage forms and plasma. The proposed method couples sensitivity (as little as 2 μg/ml can be determined) and specificity since no interference was found in the presence of common reducing sugars, antioxidants and degradation products of the vitamin. Recovery varied from 98.9 to 102.3% ± 0.2–0.5%.

Various methods have been reported for the estimation of ascorbic acid. The most widely used are the colorimetric or spectrophotometric methods depending on the reactions with 2,6-dichloroindophenol,[1,2] diazotized 4-methoxy-2-nitroaniline,[3,4] 2,4-dinitrophenylhydrazine,[5] 4-nitrobenzenediazonium fluoroborate,[6] dimethoxyquinone,[7] 2,3,5-triphenyltetrazolium chloride,[8] and phenylhydrazinium chloride.[9] A highly specific microfluorometric method is based on the reaction of dehydroascorbic acid with *o*-phenylenediamine, with a borate blank.[10] Titrations with iodine,[11] 2,6-dichloroindophenol,[12,13] and *N*-bromosuccinimide[14,15] have been reported. Differential pulse polarography has been used.[16] Ascorbic acid has also been determined as its molybdophosphate complex.[17]

Ammonium molybdate can be used for detection of ascorbic acid in paper chromatography,[18] and the present work was undertaken to examine factors influencing this reaction. The optimum conditions found were used to establish a method suitable for determining ascorbic acid in pharmaceutical dosage forms and in plasma.

EXPERIMENTAL

Reagents

Ammonium molybdate, freshly prepared 10% aqueous solution; 10% w/v sulphuric acid; 10% trichloroacetic acid solution; lactose, dextrin, starch, magnesium stearate, sodium metabisulphite, vitamins B_1, B_2, B_6, D, E, K; nicotinic acid, nicotinamide, folic acid, calcium pantothenate; rutin; calcium gluconate; copper sulphate solution; 1*M* sodium hydroxide. Stock standard ascorbic acid solution, freshly prepared in pure water; working standard prepared by dilution, to contain 0.1–0.5 mg of ascorbic acid per ml.

General procedure

Transfer 1 ml of sample solution containing 0.1–0.5 mg of ascorbic acid to a 50-ml standard flask, add 2 ml of 10% sulphuric acid and 4 ml of ammonium molybdate solution; mix and leave for 1 hr. Dilute with water to the mark and mix. Measure at 730 nm against a reagent blank prepared in the same manner but without the ascorbic acid. This blank should remain colourless for several days. Construct a calibration curve by using different concentrations (0.1–0.5 mg/ml) of ascorbic acid to develop the colour and diluting to obtain 2–10 μg/ml in the final system.

Analysis of tablets

Take a portion of the powdered tablets equivalent to 25 mg of ascorbic acid, extract it with water, filter into a suitable standard flask, then make up to volume with water. Transfer an aliquot into a suitable standard flask and apply the general procedure.

Analysis of preparations in ampoules

Dilute the contents of the ampoule to a suitable standard volume with water, and apply the general procedure to an aliquot.

RESULTS AND DISCUSSION

Development of the procedure

Preliminary experiments showed that the reaction is dependent on the ratio of sulphuric acid to ascorbic acid, the optimum being 0.2–0.4% w/v sulphuric acid in a solution containing 2–10 μg/ml concentration of the vitamin (Table 1).

For 2–10 μg of the vitamin per ml, the ammonium molybdate concentration should lie in the range 0.7–0.8% w/v in the solution measured (Table 1).

Raising the temperature accelerates the colour development, the same colour intensity being reached in 10 min at 85° and 60 min at 20°. However, interference from other reducing agents such as lactose becomes significant at higher temperature. Therefore, room temperature (20–25°) is recommended, the optimum time being 60 min (Fig. 1).

The blue colour formed is stable for about 20 hr under the specified conditions. The absorbance maxi-

Table 1. The effect of concentration of reagents on the intensity of the colour developed with ascorbic acid

Sulphuric acid, 10% *w/v* Volume, *ml*†	*A**	Ammonium molybdate, 10% *w/v* Volume, *ml*§	*A**
1.0	0.165	1.0	0.010
1.8–2.2	0.285	2.0	0.050
3.0	0.150	3.0	0.195
4.0	0.065	4.0	0.285
5.0	No colour	5.0	0.280
		6.0	Precipitation

* *A* = absorbance for 5-μg/ml ascorbic acid; average of three determinations.
† Plus 4 ml of 10% ammonium molybdate solution.
§ At a fixed sulphuric acid level of 0.4% w/v.

mum is at 720–750 nm and Beer's law is obeyed over the range 2–10 μg/ml.

Specificity of the method

Some excipients commonly added to dosage forms were found not to interfere. The recovery of ascorbic acid in the systems studied was 100.0–100.8 ± 0.1–0.4% (Table 2). The recovery was not affected even in the presence of a relatively high lactose content (1:1 ratio to ascorbic acid). The possible interference of some pharmaceuticals likely to be formulated with vitamin C has been also studied; the results are shown in Tables 2 and 3. Rutin, vitamins B_1, B_2, B_6, D, E, K, nicotinic acid, nicotinamide, folic acid and calcium pantothenate all gave no interference.

The specificity of the method for determining ascorbic acid in the presence of its decomposition products was also evaluated. Aqueous solutions of ascorbic acid which had been kept at 85° in presence of copper ions at pH 8.0 for varying periods of time were analysed. The results (Table 4) suggest that the method is suitable for monitoring the rate or degree of oxidation of the vitamin.

Determination of vitamin C in dosage forms and plasma

The results obtained are shown in Table 3. Recovery for vitamin C tablets was 98.9–102.3 ± 0.2–0.7% compared to 101.0–103.5 ± 0.8% obtained by the B.P. method.

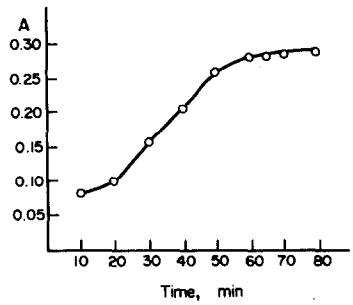

Fig. 1. The effect of time on the colour intensity (5.0-μg/ml ascorbic acid at 20°).

Table 2. Determination of 10 mg of ascorbic acid in presence of excipients, minerals and other substances usually incorporated in ascorbic acid preparations

Substance	Taken, *mg*	Ascorbic acid recovery, %*
Dextrin	5.0	100.0 ± 0.1
Magnesium stearate	5.0	100.0 ± 0.1
Lactose	10.0	100.6 ± 0.2
Starch	10.0	100.1 ± 0.1
Sodium metabisulphite	10.0	100.2 ± 0.3
Calcium gluconate	50.0	101.0 ± 0.4
Ergocalciferol	0.1	100.7 ± 0.2
Folic acid	2.0	100.4 ± 0.1
Pyridoxine, HCl	2.0	100.2 ± 0.1
Riboflavine	5.0	100.1 ± 0.3
Rutin	5.0	100.8 ± 0.3
Thiamine, HCl	10.0	100.1 ± 0.1
α-Tocopherol	10.0	100.2 ± 0.2
Menadione	10.0	100.5 ± 0.1
Calcium pantothenate	25.0	100.6 ± 0.2
Nicotinic acid	50.0	100.0 ± 0.4
Nicotinamide	50.0	100.1 ± 0.1

* Average of 5 results.

Table 3. Determination of ascorbic acid in pure form and different pharmaceutical preparations by the ammonium molybdate method, compared with the B.P.1973 method

Sample	Ammonium molybdate method Taken mg	Mean recovery %†	B.P.1973 Taken mg	Mean recovery, %†	F_{calc}§	Spiked samples (10 mg of ascorbic acid) mean recovery, %†
Pure ascorbic acid	25.0	99.2 ± 0.4	100.0	101.0 ± 0.5	1.56	
Tablets						
(1) 500 mg*	25.0	99.6 ± 0.6	100.0	102.6 ± 0.6	1.00	100.1 ± 0.2
(2) 500 mg*	25.0	98.9 ± 0.7	100.0	103.0 ± 0.5	1.96	100.0 ± 0.3
(3) 150 mg*	25.0	99.5 ± 0.7	100.0	102.6 ± 0.5	1.96	100.2 ± 0.1
(4) 160 mg*	25.0	100.8 ± 0.2	100.0	103.5 ± 0.8	16	100.0 ± 0.2
Ampoules						
(5) 500 mg*	25.0	102.3 ± 0.4	100.0	103.3 ± 0.6	2.25	100.0 ± 0.4
(6) 500 mg*	25.0	101.9 ± 0.5	100.0	102.8 ± 0.7	1.96	101.2 ± 0.5
Human plasma (4 ml + 10 mg of ascorbic acid)						102.5 ± 0.6

* Nominal content

† Average of 6 experiments.

§ F_{theory} 5.05.

(1) Cebion, Merck; (2) Redoxon, Roche; (3) Supradyn, Roche; (4) Ruta-C 60, Kahira; (5) Cevital, Nile; (6) Calcium C, Sandoz.

Table 4. Measurement of oxidation rate of 5-μg/ml ascorbic acid solution

Time, *min*	Absorbance
5.0	0.16
10.0	0.12
20.0	0.10
30.0	0.07
60.0	0.06
120.0	0.05
300.0	0.01

Experiments on human plasma spiked with vitamin C gave a recovery of 101.5 ± 0.6%. The plasma was treated with trichloroacetic acid[19] before addition of a spike of ascorbic acid and application of the method.

As shown by Table 3, the recommended method compares favourably with the B.P. 1973 method. An advantage is the sensitivity; as little as 50 μg can be determined. The method is therefore suitable for single-dose assay where the level of the vitamin is low.

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SENSITIVE SPECTROPHOTOMETRIC METHOD FOR TRACE AMOUNTS OF URANIUM

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Summary—A sensitive spectrophotometric method for the determination of uranium with Pyrogallol Red (PGR) and cetyltrimethylammonium bromide (CTAB) is described. The sensitivity of the colour reaction between uranium and Pyrogallol Red is greatly increased in the presence of cetyltrimethylammonium bromide. The blue ternary complex (λ_{max} 580 nm) has composition 1:2:4 [U(VI):PGR:CTAB] at pH 5.6. Beer's law is obeyed over the range 19.0–0.24 ppm of uranium and the molar absorptivity is 3.3×10^4 l.mole^{-1}.cm^{-1} at 620 nm. A tentative structure for the ternary complex is suggested. A simple method is suggested for evaluation of stability constants of such ternary complexes.

Pyrogallol Red (PGR) forms a violet chelate with the uranyl ion.[1,2] Other metallochromic indicators widely used for the spectrophotometric determination of uranium(VI) include PAR,[3] PAN,[4] Eriochrome Cyanine R[2] and Chromazurol S.[5,6] These colour reactions are not specific, and the sensitivity is also not adequate, especially for very small quantities of uranium(VI). In our preliminary observations it was found that the sensitivity of the uranium(VI)–PGR reaction is increased by addition of cetyltrimethylammonium bromide, owing to formation of a blue ternary complex in the pH range 4–7. There is also less interference from foreign ions. We have therefore explored the analytical value of this complex. The spectrophotometric methods proposed for evaluation of formation constants of ternary complexes are tedious and in only a few systems[7] have the formation constants of ternary complexes of surfactants been determined. We therefore propose a new simple procedure for determining such stability constants. It should be specially useful in the case of outer-sphere complexes.

EXPERIMENTAL

Reagents

A stock solution of uranyl nitrate was prepared and standardized gravimetrically by the oxine method. Working solutions were prepared by appropriate dilution. A stock solution of PGR (0.001*M*) was prepared by dissolving the required amount in 25 ml of methanol and diluting to 250 ml with redistilled water. Solutions of CTAB were prepared by dissolving the calculated amounts in hot redistilled water and cooling. Acetate buffer solutions were prepared from 0.2*M* sodium acetate and 0.2*M* acetic acid. All chemicals used were analytical-reagent grade.

RESULTS AND DISCUSSION

All experiments were done at room temperature 25° ± 1°. The total volume of the mixtures was kept at 25 ml. The order of addition of the reactants had no significant effect on the absorbance and stability of the colour, but in the studies described, the order of addition was PGR, buffer, uranyl nitrate and CTAB.

Spectral characteristics

Figure 1 shows the absorption spectra of solutions containing PGR, PGR and CTAB, PGR and UO_2^{2+}, and PGR, UO_2^{2+} and CTAB at pH 5.6. The wavelengths of maximum absorption were 530, 560, 540 and 580 nm respectively. The formation of the ternary complex is indicated by a pronounced bathochromic shift in the spectrum and a marked increase in absorbance in comparison with the binary chelate. A solution containing PGR and CTAB absorbs strongly at 580 nm but at longer wavelengths, *e.g.*, 610 and 620 nm, the absorbances of PGR and PGR–CTAB solutions are practically negligible. This is the reason for the increased sensitivity. The absorption spectra of PGR and the binary chelate solutions are almost parallel at wavelengths longer than 530 nm and so the spectrophotometric method based on the binary chelate is not sensitive.

The absorption spectra of PGR in presence of a twentyfold molar ratio of CTAB were recorded over the pH range 1.9–8.6 (Fig. 2). At between pH 6.0 and 3.3, λ_{max} is 560 nm, and outside this range gradually shifts towards the λ_{max} of PGR. For solutions containing PGR and increasing amounts of CTAB λ_{max} gradually shifts to 560 nm, becoming constant when the CTAB:PGR mole-ratio is $\geq$4:1 (Fig. 3).

Mixtures at various pH-values and containing UO_2^{2+}, PGR and CTAB in the ratio 1:2:10 were prepared and the absorption spectra were recorded (Fig. 4). The ternary complex has a constant λ_{max} at pH between 1.6 and 6.8, but the absorbance is constant only between pH 5.1 and 6.4.

Composition of the complex

The UO_2^{2+}:PGR ratio in the ternary complex was established as 1:2 by the continuous variations[8] and

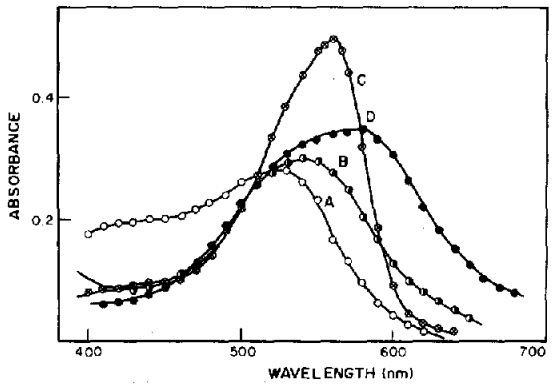


Fig. 1. *A*, PGR ($2 \times 10^{-5}M$); *B*, PGR ($2 \times 10^{-5}M$); UO_2^{2+} ($1 \times 10^{-5}M$); *C*, PGR ($2 \times 10^{-5}M$); CTAB ($4 \times 10^{-4}M$); *D*, PGR ($2 \times 10^{-5}M$), UO_2^{2+} ($1 \times 10^{-5}M$), (CTAB ($4 \times 10^{-4}M$); pH 5.6.

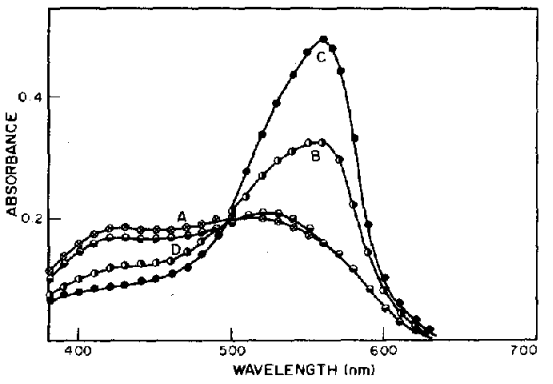


Fig. 2. PGR ($2 \times 10^{-5}M$), CTAB ($4 \times 10^{-4}M$); pH 1.9 (*A*), 3.3 (*B*), 5.6 (*C*), 8.6 (*D*).

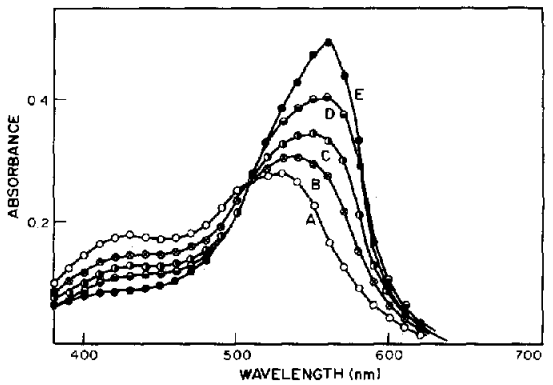


Fig. 3. PGR ($2 \times 10^{-5}M$); CTAB $2 \times 10^{-5}M$ (*A*), $4 \times 10^{-5}M$ (*B*), $6 \times 10^{-5}M$ (*C*), $8 \times 10^{-5}M$ (*D*), $1 \times 10^{-4}M$ (*E*), pH 5.6.

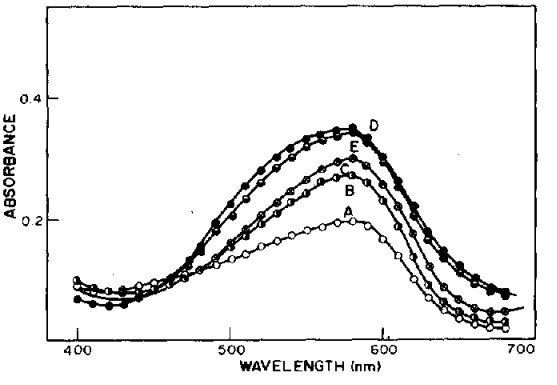
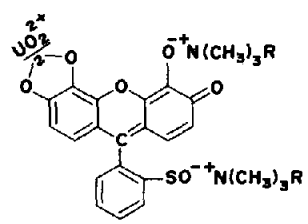


Fig. 4. PGR ($2 \times 10^{-5}M$); UO_2^{2+} ($1 \times 10^{-5}M$); CTAB ($4 \times 10^{-4}M$); pH 1.6 (*A*), 3.4 (*B*), 3.8 (*C*), 5.5 (*D*), 6.3 (*E*).

mole-ratio[9] methods in the presence of a suitable excess of CTAB. The proportion of cetyltrimethylammonium ions in the complex was determined by measuring the absorbances of mixtures containing UO_2^{2+} and PGR in the ratio 1:2 and different amounts of CTAB, and plotting the absorbances against amount of CTAB. It was found that a fourfold (molar) ratio of CTAB to complex is required for maximum colour formation. The complex is thus formulated as UO_2 $(PGR)_2(CTA)_4$.

The uranyl ion usually has co-ordination number four, which appears to be satisfied by two PGR molecules. The CTA cations would in any event be unlikely to react with the $UO_2^{2+}(PGR)_2$ chelate at the metal co-ordinating centre, and the ternary complex thus probably has the following structure:



Evaluation of stability constants

When only solution equilibria involving changes in the outer sphere have to be considered, *i.e.* in systems where the inner-sphere complexes are inert, the same experimental and calculation methods can be applied as in the case of the study of successive complex formation.[10] The ternary complex forms in a stepwise manner and can be described in terms of the following equations (charges omitted):

$$M + 2PGR \overset{k_1}{\rightleftharpoons} M(PGR)_2 \qquad (1)$$

$$M(PGR)_2 + 4CTA \overset{k_2}{\rightleftharpoons} M(PGR)_2(CTA)_4 \qquad (2)$$

$$K_1 = \frac{[M(PGR)_2]}{[M][PGR]^2} \qquad (3)$$

$$K_2 = \frac{[M(PGR)_2(CTA)_4]}{[M(PGR)_2][CTA]^4} \qquad (4)$$

The overall formation constant $\beta = K_1 K_2$. K_1 and K_2

are evaluated separately by the mole-ratio method and the expressions

$$K_1 = \frac{c_1(1-\alpha_1)}{\alpha_1 c_1(2\alpha_1 c_1)^2} \quad (5)$$

$$K_2 = \frac{c_2(1-\alpha_2)}{\alpha_2 c_2(4\alpha_2 c_2)^4} \quad (6)$$

where α_1 and α_2 are the degrees of dissociation of $M(PGR)_2$ and $M(PGR)_2(CTA)_4$ respectively, and c_1 and c_2 are the analytical concentration of UO_2^{2+} and the actual concentration of $M(PGR)_2$ respectively. The results are given in the following table.

c_1, M	α_1	log K_1	c_2, M	α_2	log K_2	log β = log K_1K_2
2×10^{-5}	0.043	12.64	1×10^{-5}	0.103	22.48	35.12

Photometric determination

For calibration, solutions (25 ml) were prepared containing a fixed amount of PGR, different amounts of uranyl nitrate solution and a constant suitable excess of CTAB, and adjusted to pH 5.6 with acetate buffer. The absorbances at 620 nm were plotted against the amount of uranyl nitrate. Beer's law was obeyed over the range 19.0 to 0.24 ppm of uranium. The molar absorptivity was found to be 3.3×10^4 $l.mole^{-1}.cm^{-1}$ at 620 nm. The relative standard deviation was 1.1% for 5 ppm of uranium. Chloride, nitrate, acetate Pt(IV), Rh(III) and Th do not interfere even in large excess. In determination of 5 ppm of uranium, the following ions interfere at the levels (ppm) given in brackets: ClO_4^-(3), PO_4^{3-}(4), SO_4^{2-}, Cu^{2+}(5), Fe^{2+}, MoO_4^{2-}, WO_4^{2-}, Ni^{2+}, Co^{2+}, VO^{2+}(6), Cr(VI) (8), In^{3+}, Ru^{3+}(9), Hg^{2+}, Ca^{2+}, Pd^{2+}(10), Cd^{2+}(11), Ga^{3+}, Zn^{2+}, Sr^{2+}(12), Y^{3+}, Al^{3+}(13), La^{3+}, Ba^{2+}, Hf^{4+}(14), Sm^{3+}(15).

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ANALYTICAL DATA

PROTONATION CONSTANT OF SOME SULPHA-DRUGS IN DIOXAN WATER MEDIUM

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Summary—The dissociation constants of some sulpha-drugs have been determined potentiometrically in 10–50% (v/v) dioxan–water media at 25° at ionic strength 0.1*M* ($NaClO_4$). Correlation of mole fraction of dioxan and p*K* gives a straight line. The p*K* values do not vary linearly with reciprocal of the dielectric constant of the medium at high percentage of dioxan.

In continuation of our studies on the sulpha-drugs,[1,2] the dissociation constants of sulphanilamide and its derivatives have been determined in 10–50% dioxan–water media at 25° and ionic strength (μ) 0.1*M* ($NaClO_4$). The effect of dielectric constant and temperature on the p*K* values has also been studied. Since the sulpha-drugs are insoluble in water the data for aqueous media are computed from the linear plot of p*K* *vs.* mole fraction of dioxan.

EXPERIMENTAL

The sulpha-drugs were used as received from the manufacturers. Dioxan was purified and stored as described by Vogel.[3] Doubly distilled water was used. Chemically pure sodium perchlorate was used to keep the ionic strength constant.

A Systronic pH-meter, type 322, was calibrated at pH 4.0 and 9.2 with potassium hydrogen phthalate and borax buffers. The U_H correction (Van Uitert and Haas[4]) was applied to the measurements.

Potentiometric titrations of, (*i*) 2.0 ml of 0.05*M* perchloric acid and (*ii*) 2.0 ml of 0.05*M* perchloric acid + 5.0 ml of 0.02*M* sulpha-drug with 0.05*M* carbonate-free sodium hydroxide were performed as described earlier.[5] The initial total volume was 50.0 ml and the desired dioxan–water composition was maintained throughout. The ionic strength was kept at 0.1*M* with 1.0*M* sodium perchlorate. An inert atmosphere was maintained inside the titration cell by passage of oxygen-free nitrogen presaturated with the solvent. Before the titration was started the contents of the titration vessel were adjusted to the desired temperature, in a thermostat.

RESULTS AND DISCUSSION

The Irving and Rossotti method[6] was used for calculation of $\bar{n}_H$ values from the titration curves (*i*) and (*ii*), and the dissociation constant, p*K*, was found by the Bjerrum half-integral method.[7] The values are also calculated by using the formula:

$$pK = pH + \log \frac{\bar{n}_H}{1 - \bar{n}_H}$$

and by plotting a graph of pH *vs.* $\log\bar{n}_H/(1 - \bar{n}_H)$. The values obtained are all in good agreement. The average values are reported in Table 1.

The p*K* value found for sulphanilamide is slightly higher than that reported earlier,[8] possibly because of the different experimental conditions.

Table 1. Dissociation constant (p*K*) of sulpha-drugs at 25 ± 0.2°C in dioxan–water media

Compound	Dioxan, % *v/v* 0*	10	20	30	40	50	*m*
Sulphanilamide	10.60	10.82	11.06	11.36	11.75	12.22	9.50
Sulphafurazole	6.15	6.45	6.70	7.10	7.52	8.10	11.20
Sulphadiazine	6.35	6.65	6.96	7.31	7.82	8.41	11.74
Sulphamethoxy pyridazine	6.75	7.02	7.30	7.68	8.12	8.70	11.08
Sulphamerazine	6.90	7.15	7.40	7.75	8.14	9.68	10.22
Sulphathiazole	7.12	7.40	7.72	8.08	8.50	9.10	11.43
Sulphaphanazole	7.50	7.72	8.05	8.40	8.80	9.32	10.52
Sulphamethizole	7.72	7.95	8.25	8.68	9.00	9.55	10.66
Sulphadimidine	7.75	8.00	8.31	8.58	9.06	9.56	10.30
Sulpha dimethoxine	8.05	8.32	8.60	8.97	9.38	9.91	10.80
Sulphapyridine	8.35	8.60	8.91	9.24	9.62	10.21	10.45
n_2	0.000	0.023	0.050	0.083	0.123	0.174	—
$1/\epsilon$	0.0127	0.0146	0.0165	0.0193	0.0235	0.0303	—

* By extrapolation (= *C* in equation $pK = mn_2 + C$).

The effect of change in dielectric constant

The degree of dissociation of an acid depends on the dielectric constant (ϵ) of the medium. In a solvent of low dielectric constant the electrostatic force between the ions is increased, which facilitates the formation of molecular species and should increase the pK value (Table 1) as reported earlier.[9,10] The dielectric constant decreases with increase in dioxan concentration in the mixtures used here.[11]

The change in pK mole fraction of dioxan (n_2) gave a linear plot obeying the relationship $pK = mn_2 + C$, where m and C are the slope and intercept (pK value at 0.0% dioxan) respectively. The values of m and C are reported in Table 1. The pK values do not vary linearly with the reciprocal ($1/\epsilon$) of the dielectric constant of the medium at high percentage of dioxan.

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DETERMINATION DES CONSTANTES D'EQUILIBRE CONDITIONNELLES ET DES CONSTANTES DE VITESSE DES REACTIONS ENTRE LE SELENIUM(IV) ET CINQ ORTHODIAMINES AROMATIQUES

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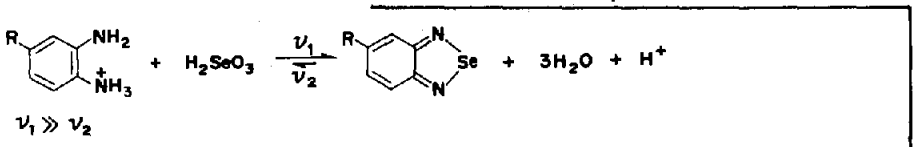
Résumé—La détermination des constantes d'équilibre conditionnelles et des constantes de vitesse, à diverses valeurs de pH, des réactions entre le sélénium(IV) et cinq orthodiamines aromatiques a permis de mettre en évidence une réaction principale, d'ordre II, qui implique la participation sélective de l'espèce monoprotonée de l'orthodiamine et de l'acide sélénieux non dissocié. L'ion monohydrogénosélénieux ou l'espèce diprotonée de l'orthodiamine peuvent prendre part à une réaction parallèle selon une cinétique plus lente. Les produits de réaction sont très stables.

Le sélénium, à l'étage d'oxydation IV, est susceptible de réagir avec des orthodiamines aromatiques pour donner un benzosélénadiazole, souvent appelé piazsélénole, utilisable pour la détermination analytique du sélénium.[1,2]

Le mécanisme réactionnel proposé empiriquement implique la participation de l'espèce monoprotonée de l'orthodiamine et de l'acide sélénieux non dissocié selon la rèaction:[3,4]



$v_1 \gg v_2$

Poursuivant nos travaux antérieurs relatifs à la détermination des constantes d'ionisation de certaines diamines aromatiques[5] et de leurs dérivés séléniés,[1] ce travail sera consacré, dans un premier temps, à la détermination spectrophotométrique des constantes d'équilibre des réactions entre le sélénium(IV) et cinq orthodiamines aromatiques, en opérant dans des conditions bien définies de température, force ionique et pH. Par la suite, nous établirons, pour chaque dérivé, une valeur de pH pour laquelle la vitesse de réaction est maximale, en suivant les variations des constantes de vitesse en fonction du pH.

PARTIE EXPERIMENTALE

Réactifs

Orthodiamines étudiées. L'orthophénylènediamine (PD) et ses dérivés 4-méthyl (4-CH_3-PD), 4-chloro (4-Cl-PD), 4,5-dichloro (4,5-diCl-PD) et 4-nitro (4-NO_2-PD). Ces dérivés ont été obtenus, purifiés et conservés selon un mode opératoire décrit précédemment;[5] ils ont été utilisés sous forme de dichlorhydrate, sauf le dérivé nitré qui a été employé sous forme dibasique. La pureté des produits a été vérifiée par dosage potentiométrique des chlorures. Les solutions de travail ($5 \cdot 10^{-4} M$) ont été préparées par dissolution d'une quantité adéquate du produit dans de l'eau bidistillée.

Acide sélénieux (Baker PA). La solution de travail ($5 \cdot 10^{-4} M$) a été préparée par dilution, à l'aide d'eau bidistillée, d'une solution mère ($10^{-2} M$) dont le titre a été vérifié par iodométrie.

Détermination spectrophotométrique des constantes d'équilibre

Méthode de Job.[6] A partir des solutions de travail placées dans des burettes, on réalise, dans des ballons jaugés de 100 ml, une série de mélanges de même concentration molaire totale en diamine et en sélénium, soit $10^{-4} M$, mais différents par la proportion relative de leurs divers constituants. La force ionique de toutes les solutions est fixée à $0{,}1 M$ à l'aide de perchlorate de sodium et le pH est ajusté à 1,5 au moyen de solutions $2 M$ d'acide perchlorique et d'hydroxyde de sodium. L'absorption de ces mélanges, placés dans un bain thermostatique à 25°, est mesurée par rapport à un réactif blanc, à une longueur d'onde précisée ci-après, jusqu'à valeur constante.

Méthode combinée de Budĕšinskỳ[3,7–9] *et de Klausen et Langmyhr.*[10] A partir des solutions de travail, on réalise une série de mélanges ayant, cette fois, la même concentration en diamine et en sélénium et des solutions de comparaison, toujours de concentration égale en diamine et en sélénium, mais dont la concentration molaire totale est de moitié plus petite. On opère dans les mêmes conditions que précédemment. L'absorption des solutions de comparaison est, en plus, mesurée dans des cellules de quartz de 2 cm pour le calcul de la constante selon la méthode de Klausen et Langmyhr.

Méthode de Budĕšinskỳ et Svec.[11] Le calcul de la constante se base sur les résultats de la méthode de Job (excès en sélénium) et de la méthode de Budesinsky (concentration équivalente en sélénium et en diamine).

La constante d'équilibre s'exprime selon l'équation:

$$K = \frac{[PIS]}{(H_2SeO_3 - [PIS])(Diamine - [PIS])}$$

[PIS] = concentration en piazsélénole à l'équilibre, H_2SeO_3 et Diamine = concentrations initiales en acide sélénieux et en diamine.

Détermination des constantes de vitesse en fonction du pH

On mesure l'absorption en fonction du temps de solutions équimoléculaires ($5 \cdot 10^{-5} M$) en sélénium et en orthodiamine, dont le pH a été ajusté à une valeur comprise entre 3,5 et 0,3. On opère dans les mêmes conditions que ci-avant.

La constante de vitesse d'une réaction d'ordre II s'exprime selon l'équation:

$$k = \frac{1}{t} \frac{x}{a(a - x)}$$

a = concentrations initiales en acide séléniéux et en diamine (égales),
x = quantité de substance ayant réagi après un temps t.

RESULTATS ET DISCUSSION

Détermination des constantes d'équilibre conditionnelles

Pour chaque dérivé, à l'exception du 4-NO_2-PD, il est aisé, en suivant l'évolution spectrale UV-visible au cours du temps de réaction entre les orthodiamines et le sélénium (à 25°, pH 1,5 et μ_i 0,1M), de sélectionner une longueur d'onde où l'absorption du dérivé sélénié formé est maximale tandis que celle de l'orthodiamine ou de l'acide sélénieux est nulle.

L'étude spectrale permet, en outre, de noter l'apparition d'un certain nombre de points isosbestiques; ceux-ci figurent au tableau 1 qui mentionne également les diverses caractéristiques spectrales observées dont l'interprétation a été donnée précédemment.[1,5]

La méthode spectrophotométrique de détermination des constantes d'équilibre à été préférée aux autres techniques, en raison des avantages qu'elle présente dans le cas particulier de la réaction étudiée.[12]

La figure 1 reprend le tracé expérimental d'une courbe de Job correspondant à l'orthophénylènediamine; l'allure de la courbe est analogue pour tous les autres dérivés. La présence d'un maximum à la valeur 0,5 de la fraction molaire en sélénium et en diamine et l'absence d'inversions de la convexité ou

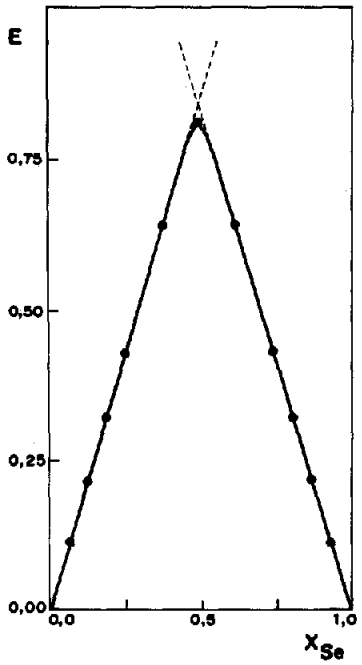


Fig. 1. Courbe de Job obtenue pour la réaction entre le sélénium(IV) et l'orthophénylènediamine (concentration totale $10^{-4} M$, 25°, pH 1,5 et μ_i 0,1M).

de parties concaves de la courbe expérimentale permet d'établir que le produit de réaction est de composition 1:1 et du type AB.[13,14] Les résultats obtenus en utilisant le tracé des tangentes de la courbe de Job figurent au tableau 2 dont l'examen indique qu'à la valeur de pH considéré, le produit de réaction est très stable. Signalons aussi que, à 25° et à pH 1,5, un temps très long (souvent deux semaines) est requis pour que la réaction soit complète.

Nous avons tenté d'obtenir des valeurs plus précises des constantes d'équilibre conditionnelles en utilisant d'autres techniques:[3,7–11] les valeurs auxquelles ces dernières ont conduit figurent au tableau 2; elles sont parfaitement compatibles entre elles mais aucune différence statistiquement valable ne peut être établie entre la stabilité des piazsélénoles obtenus. Dans tous les cas, la très grande stabilité des dérivés séléniés a nécéssairement conduit a des valeurs peu précises.

Tableau 1. Principales caractéristiques spectrales notées lors de l'étude UV-visible de la réaction entre le sélénium(IV) et les cinq diamines aromatiques (25°, pH 1,5, et μ_i 0,1M)

Dérivé	Diamine pure λ_{max}, *nm* Bande ^1L_a	Bande ^1L_b	Piazsélénole λ_{max}, *nm* Bande $\pi \rightarrow \pi^*$	Points isosbestiques, *nm*
4-CH_3-PD	232	282	335	225,5, 241, 263, 293
PD	230	280	332,5	217, 242, 261, 290,5
4-Cl-PD	236	287	338	227, 250, 269, 296,5
4,5-diCl-PD	242	299	347	231,5, 261, 267, 306
4-NO_2-PD	361	—	344	356

Tableau 2. Détermination des constantes d'équilibre conditionnelles des réactions entre le sélénium(IV) et cinq diamines aromatiques (25°, pH 1,5 et μ_i 0,1*M*)

Dérivé	$\lambda_{analytique}$ nm	Job	log *K** Buděšínský	Klausen et Langmyhr	Buděšínský et Svec
4-CH_3-PD	335	6,6	6,3	6,2	6,4
PD	332,5	7,4	7,1	7,1	7,3
4-Cl-PD	338	7,0	6,8	6,8	6,8
4,5-diCl-PD	347	6,9	6,7	6,7	6,8
4-NO_2-PD	375	7,5	6,7	6,8	7,3

* Chaque valeur représente la moyenne d'au moins 6 essais.

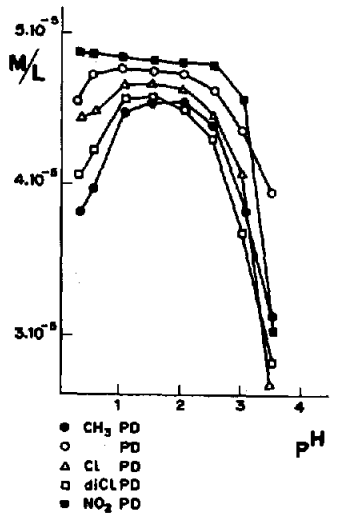


Fig. 2. Quantité en môle par litre de piazsélénole formé à l'équilibre au départ d'une solution équimoléculaire ($5 \cdot 10^{-5} M$) en diamine et en sélénium(IV) à 25°.

Il faut remarquer qu'il est malaisé de tenir compte des coefficients de réaction secondaire car, comme nous le montrons dans la suite du travail, plusieurs espèces réagissantes contribuent à la réaction dont le mécanisme apparaît alors plus complexe que celui déjà suggéré par deux auteurs.[15,16] En outre, signalons que, simultanément à la réaction étudiée, une dégradation de l'orthodiamine, très limitée en milieu acide peut se produire; sa nature et son importance sont peu connues.

En ce qui concerne le dérivé 4-NO_2, il n'a pas été possible de sélectionner une longueur d'onde où seul le piazsélénole formé absorbe; nous avons été contraints de travailler à une longueur d'onde où l'absorption de la diamine est grande par rapport à celle du piazsélénole. Ayant déterminé les coefficients d'extinction spécifique de la diamine et du piazsélénole, à la longueur d'onde et au pH considéré, nous avons pu calculer la quantité de piazsélénole formé à tout instant.

Determination des constantes de vitesse et de l'ordre de la réaction

Les réactions des cinq diamines avec le sélénium ont été suivies au cours du temps, à 25° et à des valeurs de pH variant de 0,3 à 3,5.

A la lecture de la figure 2 qui illustre le résultat de ces évolutions on constate que la zone de pH située entre 1 et 2 est optimale pour l'équilibre de la réaction directe en ce qui concerne les cinq dérivés.

La variation de pH entre 0,3 et 3,5 n'entraîne aucune modification appréciable du spectre UV-visible des piazsélénoles dont les coefficients d'extinction spécifique restent donc inchangés.[1]

Si des différences significatives dans la valeur des constantes d'équilibre ne peuvent être notées dans la zone de pH située entre 1 et 2, il n'en est pas de même pour la vitesse de la réaction qui est fortement influencée par l'acidité du milieu réactionnel.

Nous avons déterminé l'ordre et la constante de vitesse de la réaction par la méthode classique d'intégration; pour tous les dérivés, pendant environ 24 h,

Tableau 3. Valeur des constantes de vitesse d'ordre II (k), en fonction du pH pour les cinq réactions étudiées

Dérivé	pH 3,5	3,0	2,5	k, $l \cdot mole^{-1} \cdot sec^{-1}$ 2,0	1,5	1,0	0,5	0,3
4-CH_3-PD	0,15	0,33	0,67	0,90	0,82	0,38	0,11	0,07
	0,01 (10)*	0,01 (10)	0,02 (10)	0,02 (10)	0,02 (10)	0,01 (10)	0,02 (10)	0,02 (10)
PD	0,12	0,34	0,69	1,10	1,22	0,93	0,33	0,19
	0,01 (14)	0,01 (14)	0,01 (14)	0,01 (14)	0,02 (14)	0,01 (14)	0,01 (14)	0,01 (14)
4-Cl-PD	0,11	0,44	0,87	1,26	1,50	1,42	1,03	0,76
	0,01 (8)	0,01 (8)	0,02 (8)	0,01 (8)	0,02 (8)	0,01 (8)	0,01 (8)	0,02 (8)
4,5-diCl-PD	0,12	0,34	0,92	1,48	1,71	1,74	1.57	1,43
	0,03 (8)	0,03 (8)	0,03 (8)	0,03 (8)	0,02 (8)	0,03 (6)	0,04 (6)	0,06 (6)
4-NO_2-PD	0,02	0,08	0,35	0,61	0,67	0,68	0,73	0,74
	0,01 (10)	0,01 (16)	0,02 (20)	0,02 (20)	0,02 (20)	0,02 (18)	0,04 (16)	0,02 (8)

* L'écart étalon (nombre d'essais).

la constante de vitesse répond parfaitement à l'équation d'une constante de réaction chimique d'ordre II pour laquelle les concentrations des corps réagissants sont égales. Cette constatation confirme celle d'autres auteurs concernant le diaminonaphtalène[15] et le 4-CH_3-PD.[15] Le tableau 3 mentionne la valeur expérimentale des constantes de vitesse d'ordre II.

L'examen de ce tableau montre clairement que la valeur maximale de la constante de vitesse est déplacée vers des pH plus acides au fur et à mesure que la basicité de la diamine diminue.

Ayant déterminé les valeurs des constantes d'ionisation des diamines[3] et connaissant celles de l'acide sélénieux,[15,16] il nous a été possible de tracer les graphiques de distribution des espèces en fonction du pH: pour chaque dérivé, la valeur maximale de la constante de vitesse d'ordre II correspond à un pH où la quantité relative en acide sélénieux non dissocié et en diamine monoprotonée est la plus grande. La diminution de la valeur des constantes de vitesse lorsque les pH sont plus élevés est due à la diminution de la quantité d'acide sélénieux non dissocié (se transformant progressivement en monohydrogénosélèniure); la diminution en milieu plus acide est due à l'abaissement de la concentration en espèce monoprotonée (qui se transforme alors en diprotonée).

Il semble donc qu'il se produit, dans un premier temps, une réaction principale entre l'acide sélénieux non dissocié et la diamine monoprotonée; des réactions parallèles impliquant d'autres espèces ioniques se passent simultanément mais les constantes de vitesse de celles-ci sont beaucoup plus faibles et ne perturbent pas, dans un premier stade, la valeur de la constante de vitesse déterminée expérimentalement. Parmi les espèces réagissant plus lentement se trouvent l'anion monohydrogénosélèniure (explique la réaction du 4-NO_2-PD aux pH moins acides) et la forme diprotonée de la diamine (explique la réaction du 4-CH_3-PD en milieu plus acide). La réaction avec la forme dibasique de la diamine peut, selon toute vraisemblance, être exclue.

Enfin, il nous a été possible d'établir des relations entre la somme de deux constantes $\sigma_m + \sigma_p$ de Hammett[17–19] et les constantes de vitesse à un pH donné. Toutefois, le dérivé 4-NO_2-PD s'écarte totalement des tracés; nous ne pouvons, jusqu'à présent, expliquer ce phénomène.

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Summary—The conditional equilibrium and rate constants, at various pH values, of the reaction between selenium(IV) and five aromatic orthodiamines, were determined. A main reaction of second order occurs first between the monoprotonated species of the diamine and the non-dissociated selenious acid. The hydrogen selenite ion and the diprotonated diamine can also react but more slowly. The reaction products are very stable.

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ANNOTATIONS

A DISCUSSION OF SCHUBERT'S ION-EXCHANGE EQUATIONS

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Summary—A discrepancy which exists in the literature, concerning the derivation of Schubert's ion-exchange equations, is resolved.

The recent paper by Galindo and Zunino,[1] concerning the application of the ion-exchange method[2] for determining conditional stability constants of complexes, warrants discussion. Galindo and Zunino[1] erroneously claim that "an examination of Schubert's original work revealed that to derive the general ion-exchange equation he implicitly made two assumptions which are not valid". In a previous paper, Zunino *et al.*[3] stated that these alleged erroneous assumptions are:

(*i*) "that the amount of metal bound to the resin at equilibrium would be the same in the presence or in the absence of the complexant",

(*ii*) "that the free metal ion concentration in solution at equilibrium is the same in the presence or absence of the complexing anion"

and further claimed that "both wrong assumptions compensate each other" in the case of mononuclear complexes, a statement which was reiterated by Galindo and Zunino.[1] In fact, Zunino *et al.*[3] are mistaken in their conclusions and in their criticism, although there are indeed some severe communicative shortcomings in the Schubert paper.

First of all, it should be pointed out that the *two* alleged assumptions are, in fact, equivalent, and cannot lead to a valid derivation *even in the case of mononuclear complexes*, contrary to the claims in the literature.[1,3]

Establishing the precise source of the problem makes quite a story of literary detective work. The reader should refer to the original Schubert paper[2] in order to understand the dilemma (and symbols). What Schubert actually wrote was:

"The symbols to be employed in the discussion are as follows:

a = per cent of M^{+a} which has been adsorbed by the exchanger at equilibrium when the complex-forming anion, A^{-b}, is present

a_0 = same as a when A^{-b} is absent"

the intended meaning being that a_0 is the per cent of M^{+a} adsorbed by the exchanger at equilibrium when A^{-b} is absent. A misreading of these statements might suggest that the *values* of a and a_0 were the same, and thus lead to the erroneous statements of Zunino *et al.* Similar reasoning can be applied to the definitions of the fractions of M^{+a} left in solution (s and s_0).

Schubert[2] contributes further to the potential for confusion both by writing an incorrect equation and by retaining what we conclude must be a printer's error. The equation as stated by Schubert is:

$$(M_xA_y^c) = s - \frac{a_0}{\lambda_0}. \qquad (1)$$

The correct general form of the equation is:

$$(M_xA_y^c) = \frac{s - \dfrac{a}{\lambda_0}}{x} \qquad (2)$$

where the stoichiometric factor, x, is included. Use of equation (2) rather than equation (1) yields the correct general form of the Schubert equation. The term $(s - a_0/\lambda_0)$ in equation (1) is evidently a misprint as this term does not appear in subsequent parts of the derivation, but the correct expression $(s - a/\lambda_0)$ *does* occur. Thus, Schubert's equation is totally consistent if the misprint is recognized, and the stoichiometric

factor, x, is included as shown in equation (2) above. Omission of this stoichiometric factor is the essential reason that equation (8) of Schubert's paper[2] is limited to mononuclear complexes. It should be noted that a literal interpretation of the misprinted equation (1) would also lead to the erroneous interpretation of Zunino *et al.*[3]

The fallacy in the criticism of Schubert's paper[2] by Zunino *et al.*[3] has been pointed out on previous occasions.[4,5]

Finally, a major part of Galindo and Zunino's paper[1] involves modification of the ion-exchange equations to accommodate the sorption of positively charged *complexes* by the cation-exchanger. These equations had previously been derived and many such systems have already been investigated experimentally.[6,7]

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FRESH EVIDENCE FOR PROPOSED ZWITTERIONIC INTERMEDIATES

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Summary—A new selective and sensitive method for the detection of aliphatic amines has been developed with chloride-form anion-exchange resins and 2,4-dinitrotoluene. The reaction with tertiary amines can only be explained in terms of hitherto postulated zwitterionic intermediates.

The resin spot-test developed by Fujimoto[1] has several advantages. The resin beads adsorb charged complexes and give the characteristic colour of the complex. Because of the small surface area of the beads, even traces can be detected. Selectivity is increased and the charge-type of the complex can be determined.

Resin spot-tests have been widely applied to inorganic substances but their application to organic compounds has been very limited.[2] Qureshi *et al.*[3–8] have used ion-exchange beads for the detection of a number of organic functional groups.

A number of zwitterionic intermediates formed with amines in alkaline media have been postulated,[9–12] but there is little experimental evidence in support. While we were developing an ion-exchange method for the detection of amines, we found we could not explain certain experimental facts except in terms of these intermediates.

EXPERIMENTAL

Reagents

A 3–5% solution of 2,4-dinitrotoluene in distilled ethanol, and solutions of amines in conductivity water. Amberlite IR-400 (50–100 mesh) in the Cl^- form.

Procedure

Place 15–20 ion-exchange resin beads in a centrifuge tube. Add 1 drop of reagent solution and leave for 2 min. Add a drop of the test solution, let stand for 1 min, then heat in a boiling water-bath for half a minute. Add some distilled water to the tube and transfer the beads to the depression of a white spot-plate. A black to light green colour confirms the presence of an amine.

Observations

It is important to note at this juncture that when the concentration of the amine is high, then primary and secondary amines give a positive response even without heating. At first the beads turn green, the colour intensifies with time, and ultimately becomes deep blue or black. At a lower concentration of the amines heating is necessary; the beads are coloured light green and after some time they turn brown. Tertiary amines do not respond without being heated. The green colour is a distinguishing feature of the ion-exchange test and at no stage is the green colour formed in solution.

RESULTS

The following amines gave a positive result: 1,3-diaminopropane, methylamine, dimethylamine, ethylenediamine, piperidine, diethylamine, triethylamine, n-butylamine, ethanolamine and trimethylamine. A negative test was obtained with tributylamine, aniline, *o*-toluidine and diethylaniline.

A number of other organic compounds were found not to interfere with the test. They include carbohydrates (xylose, glucose, arabinose, rhamnose, fructose, maltose, lactose, galactose, melezitose, starch, sucrose); acids (acetic, picric, salicylic, phthalic, gallic, fumaric, palmitic, benzoic, cinnamic, lactic); alcohols (allyl, n-butyl, methyl, ethyl, amyl, glycerol); heterocyclic bases (pyridine); nitriles (aceto-, benzo-); aldehydes (crotonaldehyde, formaldehyde, acetaldehyde, cinnamaldehyde, benzaldehyde, salicylaldehyde, butyraldehyde, anisaldehyde, *p*-dimethylaminobenzaldehyde, *p*-dimethylaminocinnamaldehyde), ketones (cyclopentanone, cyclohexanone, benzyl methyl ketone, acetone, n-butyl isobutyl ketone, methyl n-amyl ketone, propiophenone, methyl n-propyl ketone); hydrocarbons and their derivatives (benzene, xylene, *o*-dichlorobenzene, nitrobenzene, bromobenzene, toluene); ethers (diethyl, anisole, 1,4-dioxan); amino-acids (L-lysine monochloride, DL-isoleucine, DL-α-alanine, DL-threonine, DL-serine, L-tryptophan, L-leucine, creatine, L-cysteine hydrochloride, L-proline, L-histidine monochloride, DL-phenylalanine); anilides (acetanilide); phenols (phenol, α-naphthol, β-naphthol); amides (acetamide, benzamide).

The limit of detection for a number of amines was determined and the results are summarized in Table 1.

DISCUSSION

A mechanism for the reaction of amines with 1-chloro-2,4-dinitrobenzene has been described.[13–15] However, no satisfactory explanation is given for the reaction with tertiary amines. The assumption for the formation of alkyl or aryl halides does not seem to be valid, as a carbon–nitrogen bond would not cleave so easily.

It has also been reported[16] that many compounds give brilliant colours in alkaline solutions even though they do not contain acidic hydrogen atoms, and at least two electron-attracting substituents are usually found in the *meta*-position in these molecules.

Table 1. Limit of detection for amines

Amine	Amount detected, μg
1,3-Diaminopropane	0.9
Methylamine	2
Dimethylamine	2.8
Ethylenediamine	4.5
Piperidine	5
Diethylamine	7
Triethylamine	7
n-Butylamine	10
Ethanolamine	11

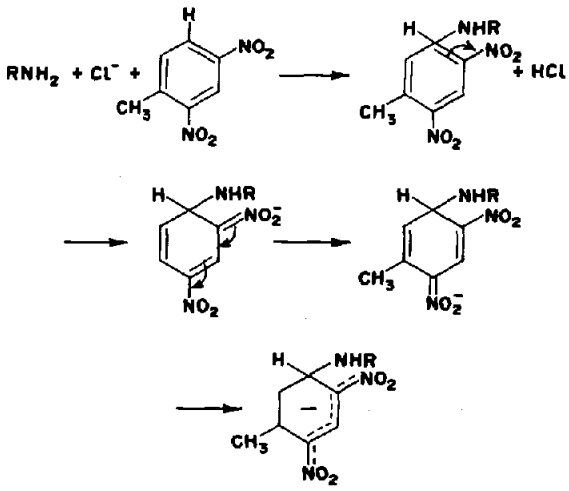
2,4-Dinitrotoluene satisfies this requirement. It has also been reported[16] that the colour reactions are related to the reaction of *m*-dinitrobenzene with activated anions in alkaline solution to give brilliantly coloured anions. 2,4-Dinitrotoluene has considerable similarity to *m*-dinitrobenzene.

Here the amines themselves provide the alkaline medium. This is why aromatic amines, which have a much lower basicity than their aliphatic counterparts, do not give this test. This is shown by the behaviour of piperidine (positive test) and pyridine (negative test).

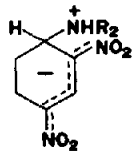
The observed fact that the complex is adsorbed on an anion-exchanger in the Cl^- form confirms the assumption that the complex is negatively charged. The anion is held by electrostatic attraction to the positively-charged matrix of the exchanger.

The mechanism shown in Scheme 1 is proposed for primary and secondary amines. The initial green colour can be attributed to a zwitterion of the type shown in Scheme 2. However, the positive charge on the matrix repels the positive charge on the nitrogen atom and the zwitterion is converted into the anion shown in Scheme 1 and HCl is removed. The colour of the beads is turned to deep blue or black. Hence the zwitterion is a green species and the anion is a deep blue or black species.

In the case of tertiary amines the zwitterion shown in Scheme 3(a) is formed. Here the positive charge is balanced by the negative charge of Cl^- and the

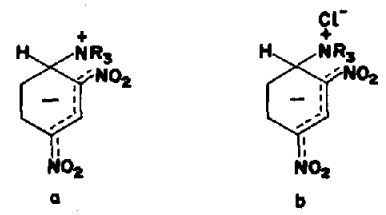


Scheme 1. Reaction with primary and secondary amines.



Scheme 2. Zwitterion with primary and secondary amines.

species shown in Scheme 3(b) may be formed. Hence the initial zwitterion loses its identity and more closely resembles the anion.



Scheme 3. (a) Zwitterion with tertiary amine, (b) Cl^- balancing positive charge.

Two factors seem to contribute to the final result, basicity and steric factors. In trimethylamine the basicity outweighs the steric factors and hence we get a colour even in the cold. In the case of triethylamine the basicity dominates only at elevated temperatures and hence we get a colour on heating. For tributylamine the steric factor outweighs the basicity even at elevated temperatures and hence we do not obtain a colour even on heating.

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LETTER TO THE EDITOR

APPROACHES USED IN DEDUCING SCHUBERT'S ION-EXCHANGE EQUATIONS

SIR,

MacCarthy and Mark[1] have criticized our article[2] wherein some limiting factors in the application of Schubert's ion-exchange method are studied, and repeat the criticisms they have already given elsewhere[3] (which were opportunely answered[4]).

They claim[1] that Schubert's original paper[5] contains "severe communicative shortcomings" and conclude that "Schubert's equation is totally consistent if the misprint is recognized, and the stoichiometric factor, x, is included". Of course, under these circumstances there will be more than one possible interpretation, depending on what might be supposed were Schubert's thoughts in writing his paper and also on whether it might be considered there is a misprint or not, and this is rather a subjective matter.

On that basis we can accept MacCarthy and Mark's views but at the same time we must state that our reasoning did not arise from misreading Schubert's paper but from an interpretation based on a different point of view. Their suggestion that we could have misunderstood the definition of a and a_o we consider is especially irrelevant.

It has already been well established that Schubert's equations (7) and (8) in the original paper[5] are incorrect, but his equation (9) is correct because the previous error cancels. MacCarthy and Mark[1] state that "omission of this stoichiometric factor is the essential reason that equation (8) of Schubert's paper is limited to mononuclear complexes". In this respect we suggest the reading of our previous answer;[4] besides, it is of interest to examine how Schubert actually worked out the stoichiometric factor in his subsequent paper[6] rather than examining again the original one, which appears to have suffered from poor presentation.

Schubert, Russell and Myers[6] in 1950 simplified the original Schubert equation to make the method applicable to ML_y-type complexes. The simplified equation they gave has been the most widely used for determining apparent stability constants by the ion-exchange method.[7] In that paper Schubert *et al.* stated under "Pertinent Equations":

"The dissociation reaction for the complex ion, $(K_x A_y)^c$, or its equivalent $(MA_{y/x})^c$, is $(MA_n)^c \rightleftharpoons M^a + n\,A^b$. In these expressions K and A represent cationic and anionic groups, x and y the number of such groups in the complex, a and b the charges on the dissociated cations and anions, respectively, c the net charge on the complex, and $n = y/x$. The dissociation constant, K_c, for the complex ion follows from the law of mass action: $K_c = (M^a)\,(A^b)^n / (MA_n)^c$".

With this simple algebraic artifact Schubert *et al.* got rid of polynuclear complex $M_x A_y$ to end up with the mononuclear complex MA_n. Elementary algebra appeare to say that this step is correct but from the chemical point of view we think it is incorrect, since it involves a transformation of structure in the complex and ignores the fact that the average number of bound ligands (as a function of the free ligand concentration) will depend on the metal ion concentration whereas for mononuclear complexes it is independent of it.[8] It is now very well established that mononuclear and polynuclear complexes have different properties, fundamentally because of differences in their structures. After 1950 Schubert

and co-workers investigated only mononuclear complexes and never again included symbols in the nomenclature which could have implied the possibility of applying their equations to M_xA_y-type complexes, as Schubert did in the original work.[5]

In the late sixties studies of complexes of the M_xL and M_xL_y types became increasingly important, especially in relation to organic macromolecules in soil.[9] Our earlier discussion of Schubert's equations[10] was intended to demonstrate that they were applicable only to mononuclear complexes and, at the same time, to deduce an alternative equation valid for the general case, since the only one available at that time (Schubert's equation 8,[5] was incorrect, whatever the reason for it. The main purpose of our paper in Talanta[2] was to give an analytical tool useful for choosing the most appropriate concentration range for the complexant to be used in connection with the ion-exchange method. Reference to the Schubert equation was included for completeness.

We hope that the problem has now been sufficiently discussed to prevent future misinterpretation, and that no further debate will be necessary.

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The Editorial Board and Publisher of *Talanta* take great pleasure in announcing that the Louis Gordon Memorial Award for the best-written paper published in *Talanta* in 1978 is made to E. VAN HOYE, F. ADAMS and R. GIJBELS, University of Antwerp, for their paper "Sensitivity calibration for the spark-source mass-spectrometric analysis of aluminium and its alloys" (*Talanta*, 1978, **25**, 73).

Professor TAITIRO FUJINAGA presenting the Louis Gordon Memorial Award for 1977 to IAWO TSUKAHARA.

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The first award is being made retroactively for the years 1977 and 1978, and goes to J. W. Mitchell and V. Gibbs for their paper "Quantitative Ion-Exchange Separation of Submicrogram Amounts of Iron from Phosphate Medium" (*Talanta*, 1977, **24**, 741).

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EDITORIAL

UTILITY AND FUTILITY

It is now 45 years since Lundell wrote his famous paper "On the Analysis of Things as They Are" (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 231), and though it is treasured by most of those who take the trouble to read it, a survey of current literature leaves the impression that these are few in number. Readers see only the papers that are thought acceptable by the referees and the editors, and remain unaware of the papers that are refused. They therefore see a somewhat biased picture of the present state of analytical research, and may deem it to be healthier than it is. Analysis is above all a severely practical branch of science, and should be judged by its utility in solving practical everyday problems. Though a good deal of analytical research is undoubtedly inventive, ingenious and innovatory in this respect, too large a proportion is unimaginative, works over old ground that has long been exhausted, and produces procedures that are non-selective, subject to unacceptably large errors, and applicable to such a restricted range of samples that they are practically worthless.

Development of such procedures may be justified on the grounds that it is a convenient and well-proven method of training students in research methods, and on-one would quarrel with this view provided no attempt were made to publish the results. The objection is to the needless publication of methods that are in reality inferior to the ones they seek to replace. The main source of such papers is research on organic reagents. In the early days there was great hope that a specific reagent could be found for each element. It has long been realized that this was only a dream, but the world is evidently full of optimists who refuse to believe it and go on turning out new reagents that are in no way superior to their predecessors, and sometimes inferior. Because of the nature of the platinum metals and first row transition metals, new reagents will usually react with several of these, resulting in further proliferation of papers (one per element–reagent combination) describing the effects. Solvent extraction and ion-exchange also provide ample opportunity for permutation and combination, and though useful results can be obtained they are frequently accompanied by a great deal of relatively useless information. Polarographic examination of weak complexes between organic acids and various metal ions is another fruitful source of papers which often serve only the function of filling gaps (sometimes unreliably) in the compilations of data. The complexes themselves are seldom of analytical use, though data on them may be of interest in bio-inorganic chemistry.

It may be argued that *any* new knowledge is of value simply because it is something added to our store of knowledge. This may have been true in the earliest days of organized research, when insufficient was known for value judgements to be formed, but it can scarcely be justified today. Much of the material that is published in the modern scientific literature seems to be akin to knowing how many research workers died in development of the method of processing cassava to give an edible product—interesting as a curiosity but definitely not useful.

We earnestly beseech our fellow-workers to consider carefully (a) the objectives of their current research, (b) the practical utility of the results obtained and (c) whether *not* publishing would be a loss to the world at large and of science in particular. By all means let research students be trained as before, but the results of their work should be offered for publication only if they meet the criteria outlined above.

We couple this appeal with another to industry as well as our colleagues. Industry frequently has problems but not the time or facilities to solve them. The academic research centres could provide both the time and the workers necessary. True, there are problems of confidentiality in connection with processes, but these could be overcome with good will on both sides. Certainly neither party can afford to neglect the opportunities available for a truly fruitful collaboration.

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BOOK REVIEW

COMPREHENSIVE ORGANIC CHEMISTRY

The Synthesis and Reactions of Organic Compounds

Chairman of the Editorial Board: Sir Derek Barton, FRS
Deputy Chairman: W. David Ollis, FRS

Reviewed by Lord Todd, PRS, *Cambridge*:
Volume 1 (Stereochemistry, Hydrocarbons, Halo Compounds, Oxygen Compounds; edited by J. F. Stoddart, *Sheffield*)

When I was a young doctoral research worker in organic chemistry—and that was nearly fifty years ago—I, like all practising organic chemists of the day, had quite a problem on my hands. Ours was a large and growing subject with a high factual content and a rather primitive theoretical base. As a result it was difficult to systematise or abbreviate by generalisation. To master it and to use it required real familiarity with the various compound types and with reactions and methods. To this end the practising organic chemist needed not just a simple textbook (of which quite a few existed) but something a good deal more comprehensive which he could have on his own bookshelf. He needed a source book from which he could quickly get basic information on the behaviour and reactions of organic compounds and in which he could browse and increase not just his factual knowledge but also his chemical insight. But no single work existed to fill this need. Of course there were vast encyclopaedic works like Beilstein and many individual monographs but no single comprehensive work on a reasonable scale. And so we fell back to using two books: (a) a general text, usually Karrer, *Lehrbuch der Organischen Chemie*, and (b) a book on methods like Houben–Weyl, *Methoden der Organischen Chemie* or, if we were hard up, the shorter and cheaper Meyer, *Analyse und Konstitutionsermittlung Organischer Verbindungen*. During the fifty years since then the situation has not improved. Certainly we have extensive and detailed works like Rodd's *Chemistry of Carbon Compounds* which is an invaluable source of factual information, but is so large that it can be regarded as essentially a library work of reference rather than one which individuals keep on their own shelves and read regularly. This is perhaps the inevitable consequence of the staggering growth of organic chemistry during the past half-century; this growth no doubt accounts in part for the enormous expansion of Houben–Weyl. The 3rd Edition of that work, which ran to four substantial volumes, although immensely valuable was close to the limit in size for the individual reader; but the new 4th Edition is so enormous that it is quite beyond the pocket of the individual (and perhaps even of some libraries) and has lost some of its original character. Both of these reference works incidentally have a major defect inherent in their slow rate of publication: earlier volumes of each are not infrequently out-of-date before some later ones appear.

There remains therefore a gap in the literature of organic chemistry which is even more serious today than it was in the past. For this reason one must applaud the task which the editors and publishers of *Comprehensive Organic Chemistry* have set themselves in trying to fill this gap and by undertaking to publish the entire work on a mid-1977

coverage deadline during the first 3 months of next year. If this is achieved it will be a spectacular technical achievement. The intention is to issue the whole work in 6 volumes of around 1200 pages each and this article is specifically concerned with Volume 1. My comments on the work as a whole rest therefore on the assumption that Volume 1 is typical of them all; from its layout, its list of contents, and my perusal of the individual chapters this would seem a not unreasonable assumption to make.

I confess that I have been much impressed by Volume 1, largely, of course, because it meets my criteria for a personal reference text for the practising organic chemist. The coverage is on orthodox lines and comprises aliphatic and alicyclic hydrocarbons, arenes, halo-compounds, alcohols, phenols, carbonyl compounds and ethers. It contains the essential factual matter on individual groups of compounds but employs what I would call the Houben–Weyl approach to methods and reactions modernised on the basis of mechanistic ideas and it gives copious and, on the whole, well-chosen references to more detailed sources of information. Volume 1 includes, in addition to chapters on individual compound groups, others on theoretical topics such as stereochemistry and aromaticity which are dealt with in a thoroughly up-to-date manner. On first approaching it I felt the opening chapter on stereochemistry was curiously located, but on further reflection I think that this may be rather unfair. This book is in no sense an introductory text on organic chemistry for undergraduates and to give a comprehensive treatment of modern stereochemistry as a kind of introduction may well be desirable. One criticism which I would make is that the balance is not in my opinion always perfect; for instance I find it hard to believe that quinones warrant no more than 12 pages (and these mainly on benzoquinones) whereas 40 pages are devoted to annulenes. Of course, there are always differences of opinion on the relative importance of individual topics just as there are differences in style of presentation by individual authors, but although there is, here and there, a little unevenness in style, the editors have done such an excellent job in controlling general treatment of topics that any unevenness is not obtrusive. Some other minor criticisms could be made but they would not affect my view that this promises to be a real contribution to the literature of organic chemistry. It is not in competition with the encyclopaedic works of reference which we have but is a comprehensive first source to which the chemist can turn for information and in which he can browse for inspiration. If the other five volumes adequately match the first then *Comprehensive Organic Chemistry* will fill a long-felt need and should be a success.

Reviewed by G. Ourisson, *Strasbourg*:
Volume 2 (Nitrogen Compounds, Carboxylic Acids, Phosphorus Compounds; edited by I. O. Sutherland, *Liverpool*).

The present volume is probably typical of the complete series. It is "medium-sized", has a very wide coverage, relies heavily on existing reviews and books, and is definitely up-to-date.

Its medium size is in line with the British tradition of Rodd's *Chemistry of Carbon Compounds*, and runs opposite to the German ideal of the exhaustive Handbuch, as well as to the American one of the specialised monograph. This intermediate character makes it certainly easier for the reader to scan for the essential points in a domain new to him, at a level deeper than that made accessible by textbooks, and with the provision of key references to the primary literature, and to specialised reviews. In most chapters, the bibliography contains the essential recent books, mentions extensively chemical Reviews or Organic Reactions, Houben–Weyl or Patai, in brief does not make-believe that the author has read all the primary references quoted, and only primary literature. This is of course all to the advantage of the reader, who will certainly want to begin his reading by such reviews. Let us note at this stage that the latest references mentioned are from 1976 to 1977, and that in most chapters, the patent literature is practically ignored. (In this

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Spectrophotometric determination of cerium(IV) with Solochrome Black 6B: V. KRISHNA REDDY and D. VENKATA REDDY. (3 October 1978)

A new titrimetric method for the milligram determination of ethacrynic acid in pharmaceutical preparation: S. SHUKLA, V. N. PATHAK and I. C. SHUKLA. (4 October 1978)

A new highly sensitive spectrophotometric method for determination of trace amounts of uranium: OM PRAKASH, S. KUMAR and S. P. MUSHRAN. (4 October 1978)

Spectrophotometric determination of calcium, magnesium and phosphate in Ca and Mg-hydroxylapatites: HEMADRI CH. PANDEY and PREMA N. PATEL. (9 October 1978)

Stability constants and molar absorptivities for complexes of chromium(III) and cobalt(II) with 2-pyridylmethanamine: JOSEPH R. SIEFKER and REKHA D. SHAH. (9 October 1978)

Spectrophotometric determination of *N-o*-tolylbenzohydroxamic acid with vanadium(V): V. C. KOSHY and S. G. TANDON. (10 October 1978)

Reduction of Fe(III), V(V) and Cr(VI) on tetrachlorohydroquinone and oxidation of Fe(II), V(II) and Cr(II) on tetrachloroquinone columns: S. K. MANDAL and B. R. SANT. (10 October 1978)

A discussion of Schubert's ion-exchange equations: PATRICK MACCARTHY and HARRY B. MARK, JR. (11 October 1978)

Differential determination of tellurium(IV) and tellurium(VI) with sodium diethyldithiocarbamate, ammonium pyrrolidinedithiocarbamate and dithizone by atomic-absorption spectrophotometry with a carbon-tube atomizer: TOSHIHIKO KAMADA, NORIO SUGITA and YUROKU YAMAMOTO. (12 October 1978)

The determination of FeS_2 in Venezuelan laterites after a sulphurization process: J. J. LA BRECQUE and P. A. ROSALES. (20 September 1978)

Schnelltests zur Leistungsfähigkeit von Bestimmungsverfahren: G. GOTTSCHALK. (4 October 1978)

Polarographic behaviour of Th(IV) in the presence of some ionic and non-ionic surfactants vis-à-vis their influence on the kinetics of the electrode reaction: M. C. DUBEY and MUKHTAR SINGH. (18 October 1978)

A general method for coulometric titration of alkylanilines with bromine: L.-A. TRUEDSSON and B. E. F. SMITH. (19 October 1978)

Coulometric titration of anilines, mainly containing deactivating functional groups, with bromine: L.-A. TRUEDSSON. (19 October 1978)

Investigation on the extraction equilibrium of vanadium–PAR complex from aqueous solutions with a chloroform solution of quaternary ammonium chloride: E. PAPP and J. INCZÉDY. (24 October 1978)

Protonation constant of some sulpha-drugs in dioxan–water medium: KEEMTI LAL. (24 October 1978)

Coulometric investigation of the drying conditions of bauxites for chemical analysis: TAKAYOSHI YOSHIMORI, YOSHIHIRO ASANO and YÛICHI HATTORI. (24 October 1978)

Investigation of fluoride complexes of aluminium in water–ethyl alcohol system: M. TOMAŠEVIĆ-ČANOVIĆ and D. VESELINOVIĆ. (26 October 1978)

Handling of electronic absorption spectra with a desk top computer—I: A fully automatic spectrophotometric titration system with on-line data acquisition: GERNOT HÄNISCH, THOMAS A. KADEN and ANDREAS D. ZUBERBÜHLER. (30 October 1978)

Spark-source mass-spectrometric sensitivity factors for elements in a graphite matrix: B. VANDERBORGHT and R. VAN GRIEKEN. (31 October 1978)

Determination of small amounts of boron by radiation decomposition of chloroacetic acid solution: M. H. YANG, C. L. TSENG and G. TÖLG. (1 November 1978)

Spectrophotometric determination of tetrazene in primers and primer mixes by use of resorcinol: GEORGE NORWITZ and PETER N. KELIHER. (18 October 1978)

Determination of small concentrations of HCl by derivatization: A problem and how it might be solved: B. VIERKORN-RUDOLPH, H. M. BIEHL, P. MATUSCA and K. BÄCHMANN. (3 November 1978)

Metal chelates of phosphonate-containing ligands—I: Stability of some *N,N,N',N'*-ethylenediaminetetra(methylenephosphonic acid) metal chelates: E. N. RIZKALLA and M. T. M. ZAKI. (3 November 1978)

Erprobung und Vergleich von Aufschlußverfahren zur Spurenanalyse in Erdölprodukten an den Beispielen Calcium, Vanadium und Zink: W. Ross and F. Umland. (30 October 1978)

Kinetisch-katalytische Bestimmungen in einem Zweiphasensystem unter Verwendung eines Fallrohres: Herbert Weisz and Wolfgang Meiners. (19 October 1978)

Determination of sulphur by electrolytic hydrogenation: Mieczyslaw Wroński. (6 November 1978)

The stability constants of the aqueous chloro complexes of bivalent zinc, cadmium and mercury, determined by solvent extraction with tri-n-octylphosphine oxide: Taichi Sato and Takato Nakamura. (6 November 1978)

The X-ray fluorescence analysis of Cu–Pb–Zn ores: Rajeev, S. C. Srivastava and M. K. Ghosh. (7 November 1978)

Zero-current bipotentiometric end-point indication with pretreated electrodes—V: Use of pretreated tin oxide electrodes: L. Kékedy and F. Kormos. (7 November 1978)

Determination of chloramphenicol in pharmaceutical preparations by the cadmium ion-selective electrode, spectrophotometry and atomic-absorption spectrometry: Saad S. M. Hassan and M. H. Eldesouki. (7 November 1978)

Determination of submicrogram amounts of vanadium in biological materials by *N*-cinnamoyl-2,3-xylylhydroxylylamine extraction and flameless atomic-absorption spectrometry using a pyrolytic-graphite-coated atomizer: Mutsuo Ishizaki and Seiichi Ueno. (7 November 1978)

Vergleichende Untersuchung an Reagentien zur spektralphotometrischen Bestimmung von Zink: G. Ackermann and J. Köthe. (9 November 1978)

Talanta, Vol. 26, pp. I–III
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PAPERS RECEIVED

On the use of rubidium 12-tungstoarsenate membrane electrode in the potentiometric determination of rubidium: AJAY K. JAIN, S. K. SRIVASTAVA, RAJ P. SINGH and SUSHMA AGRAWAL. (18 April 1979)

Simultaneous microdetermination of sulphur and phosphorus in organic compounds: S. W. BISHARA and F. M. EL-SAMMAN. (18 April 1979)

Small scale determination of a few azo compounds with *N*-bromosaccharin: RAVI PRAKASH, Km. S. R. SHUKLA and I. C. SHUKLA. (18 April 1979)

Spectrophotometric microdetermination of chromium(VI) with resacetophenone oxime: G. ABDUL HUQ and S. BRAHMAJI RAO. (18 April 1979)

Non-aqueous titrimetric determination of *N*-*p*-chlorophenylbenzohydroxamic acids: Visual and potentiometric titration in dimethyl formamide: R. D. ROSHANIA and Y. K. AGRAWAL. (23 April 1979)

Application of simplified complementary tristimulus colorimetry to chemical kinetics in solution—II: Evaluation of optimum time: R. TAWA and S. HIROSE. (23 April 1979)

Application of simplified complementary tristimulus colorimetry to chemical kinetics in solution—III: Determination of two parallel or consecutive first-order rate constants: R. TAWA and S. HIROSE. (23 April 1979)

Effect of hydrogen-ion concentration on the extraction of cobalt, nickel, cadmium and lead with APDC/MIBK. Time stability of the extracts: INGEMAR DELLIEN and LEIF PERSSON. (23 April 1979)

The mechanism of interaction between molybdogermanic acid and the Crystal Violet: F. V. MIRZOYAN, V. M. TARAYAN, E. KH. HAIRIYAN and N. A. GRIGORIAN. (23 April 1979)

Spectral bandwidth in plant chlorophyll determinations: MALCOLM S. CRESSER and EILEEN J. O'NEILL. (24 April 1979)

Metal oxide reduction: A low-temperature reaction with graphite in flameless atomic-absorption spectrometry: R. H. EKLUND and J. A. HOLCOMBE. (26 March 1979)

Study of the oxidation of ethylenediaminetetra-acetic acid with lead dioxide suspension in sulphuric acid: SHINICHI ITO, TOSHIO MATSUDA and TOYOSHI NAGAI. (25 April 1979)

Determination of bismuth in ores, concentrates and non-ferrons alloys by atomic-absorption spectrophotometry after separation by diethyldithiocarbamate extraction or iron collection: ELSIE M. DONALDSON. (25 April 1979)

Determination of cadmium and lead in urine and other biological samples by graphite-furnace atomic-absorption spectrometry: PATRICIA A. LEGOTTE, WILLIAM C. ROSA and DORIS C. SUTTON. (18 April 1979)

***p*-Chloro-substituted cinnamohydroxamic acids as analytical reagents for cerium: Spectrophotometric determination with *N*-phenyl-*p*-chlorocinnamohydroxamic acid:** R. K. JAIN and Y. K. AGRAWAL. (25 April 1979)

Search for the optimum conditions of extraction of transition metal complexes with pyridine derivatives: Extraction of the Co(II), Ni(II), Cu(II) and Zn(II) complexes of 3,4-dimethylpyridine: B. LENARCIK and E. BEZAK. (26 April 1979)

Dichloramine-B as a new redox titrant in non-aqueous or partially aqueous media: H. S. YATHIRAJAN, D. S. MAHADEVAPPA and RANGASWAMY. (27 April 1979)

Carl Friedrich Mohr and analytical chemistry in Germany: FERENC SZABADVÁRY and ROBERT A. CHALMERS. (20 April 1979)

The influence of pH and complex formation on the ASV peaks of Pb, Cu and Cd: E. A. SCHONBERGER and W. F. PICKERING. (2 May 1979)

A simple and sensitive new spot-test for iron: ALEXANDER J. PANDELL, ROBERT A. MONTGOMERY and RICHARD A. MEISSNER. (25 April 1979)

The use of approximation formulae in calculations of acid–base equilibria—II: Salts of mono- and diprotic acids: HISATAKE NARASAKI. (2 May 1979)

The use of approximation formulae in calculations of acid–base equilibria—III: Mixtures of mono- or diprotic acids and their salts: HISATAKE NARASAKI. (2 May 1979)

Analytical utility of 2-halopyridinium salts—II. Acidimetric determination of thiol groups: EDWARD BALD. (3 May 1979)

Determination of stability constants from experimental photometric curves: CHARLOTTE VON HAARTMAN. (3 May 1979)

New specific spot-test for the detection and semiquantitative determination of α-ketoglutaric acid: H. S. RATHORE, M. N. AKHTAR and S. K. SHARMA. (3 May 1979)

Determination of thiocarbamides: D. S. SABDE and R. B. KHARAT. (3 May 1979)

Precision and linearity of determination at high concentrations in atomic-absorption spectrometry: M. S. EPSTEIN and J. D. WINEFORDNER. (3 May 1979)

Spectrophotometric determination of uranium with anthranilic acid and Rhodamine 6G: T. V. RAMAKRISHNA and R. S. SHREEDHARA MURTHY. (3 May 1979)

***N*-(2,5-Dimethyl)phenyl-*p*-toluimidoylphenylhydrazine as a new chromogenic reagent for copper(II):** K. S. PATEL, R. S. KHARSAN, V. K. SAXENA and R. K. MISHRA. (4 May 1979)

Liquid-membrane type dodecylbenzenesulphonate ion-selective electrode employing Victoria Blue as the counter-ion: T. KOBAYASHI, M. KATAOKA and T. KAMBARA. (8 May 1979)

Quantitative separation of gallium from zinc, copper, indium, iron(III) and other elements by cation-exchange chromatography in hydrobromic acid–acetone: F. W. E. STRELOW. (8 May 1979)

Determination of polycyclic aromatic hydrocarbons in industrial waste water at the ppM level: R. KADAR, K. NAGY and D. FREMSTAD. (8 May 1979)

Complexometric determination of magnesium in presence of phosphate and chromate: S. K. VIJAYALAKSHAMMA and H. S. SATHYANARAYANA RAO. (8 May 1979)

Hydroxamic acids: Reagents for solvent extraction and spectrophotometric determination of metals: Y. K. AGRAWAL and S. A. PATEL. (9 May 1979)

A new chelate-forming resin bearing mercapto and azo groups: MASAHIKO CHIKUMA, MORIO NAKAYAMA, TOMOO TANAKA and HISASHI TANAKA. (9 May 1979)

Determination of thallium and lead in cadmium salts by anodic-stripping voltammetry with inhibition of cadmium electrochemical activity by addition of surfactants: ZENON ŁUKASZEWSKI, MARIA KRYSTYNA PAWLAK and ALEKSANDER CISZEWSKI. (10 May 1979)

Metal chelates of phosphonate-containing ligands—V: Stability of some 1-hydroxyethane-1,1-diphosphonic acid metal chelates: E. N. RIZKALLA, M. T. M. ZAKI and M. I. ISMAIL. (10 May 1979)

Determination of ppM levels of sulphide by a chemiluminescent reaction: J. L. BURGUERA and ALAN TOWNSHEND. (10 May 1979)

The separation of inorganic bromides by adsorption gas chromatography: S. TSALAS and K. BÄCHMANN. (11 May 1979)

Flow-injection analysis for traces of lead and cadmium by solvent extraction with dithizone: O. KLINGHOFFER, J. RŮŽIČKA and E. H. HANSEN. (11 May 1979)

Hydroxide complexes of lanthanides—II: Samarium(III) in perchlorate medium: J. KRAGTEN and L. G. DECNOP-WEEVER. (15 May 1979)

Solution equilibria studies of mixed complexes involving biologically active ligands [Ni(II), Zn(II) or Cd(II)–picolinic acid–α-amino-acids]: B. P. SINGH, H. S. VERMA, G. S. MALIK and S. P. SINGH. (16 May 1979)

Identification and estimation of proteins by using a modified biuret-reagent: A. BHAGAVANULU, P. APPALA RAJU, P. L. NARASHIMHAM and P. V. BHIRAVAMURTY. (16 May 1979)

Amperometric determination of opium and strychnos alkaloids with potassium thallium(I) iodide reagent: N. V. RAMA RAO and S. N. TANDON. (16 May 1979)

Complexometric photometric titrations without an indicator: CHARLOTTE VON HAARTMAN. (17 May 1979)

Iodine trichloride as an analytical reagent: Determination of some organic compounds: KRISHNA K. VERMA. (18 May 1979)

Extraction of zinc and cadmium thiocyanate complexes in the presence of pyridine, and some metal-ion separations: DEVENDRA SINGH, J. M. SINGH, O. V. SINGH and S. N. TANDON. (18 May 1979)

A spectrophotometric determination of europium in lanthanide and other mixtures by use of Methylene Blue: SWAGATA BHATTACHARYA, SAMUEL J. LYLE and REZA MAGHZIAN. (21 May 1979)

Use of acetylacetone as an extractant in separation of niobium and tantalum from a mixture in hydrofluoric and nitric acid medium: N. R. DAS and S. N. BHATTACHARYA. (22 May 1979)

Studies on the interaction of some metals with *N*-4-methylacetophenacylidene-*o*-methoxyaniline: V. SINGH, SMT. C. SINGH and P. SINGH. (22 May 1979)

Analytical applications of *m*-toluidinyloxamic acid: Estimations of some lanthanons and their separation from other metal ions by use of masking agents: V. K. SHARMA, R. C. SHARMA and G. K. CHATURVEDI. (25 May 1979)

Studies on Brilliant Green and Solochrome Red B—X: Development of the spectrophotometric method for iron: A. A. ELSIRAFY. (25 May 1979)

Spectrophotometric determination of traces of lead by ternary complex formation: T. PRASADA RAO and T. V. RAMAKRISHNA. (25 May 1979)

On the complex formation between Cd(II) and EDTA: MOHAMMED JAWAID. (28 May 1979)

Correction factors for the glass electrode in aqueous ethanol: Y. K. AGRAWAL. (28 May 1979)

Determination of trace quantities of selenium by indirect atomic-absorption spectrophotometry: M. VIJAYAKUMAR, T. V. RAMAKRISHNA and G. ARAVAMUDAN. (29 May 1979)

Fluorimetric determination of trace quantities of mercury by ion-association with Rhodamine 6G in the presence of iodide: M. VIJAYAKUMAR, T. V. RAMAKRISHNA and G. ARAVAMUDAN. (29 May 1979)

Microionization constants of sulphonamides: H. SAKURAI and T. ISHIMITSU. (30 May 1979)

Austausch mit cyclischen Polyethern als Ankergruppen—I: Herstellung und Charakterisierung: E. BLASIUS, K.-P. JANZEN, M. KELLER, H. LANDER, T. NGUYEN-TIEN and G. SCHOLTEN. (7 March 1979)

Austausch mit cyclischen Polyethern als Ankergruppen—II: Anwendungen: E. BLASIUS, K.-P. JANZEN, W. ADRIAN, W. KLEIN, H. KLOTZ, H. LUXENBURGER, E. MERNKE, V. B. NGUYEN, T. NGUYEN-TIEN, R. RAUSCH, J. STOCKEMER and A. TOUSSAINT. (7 March 1979)

A complexometric method for the determination of small amounts of an alkaline earth in mixture with other metals: ERLAND JOHANSSON and ÅKE OLIN. (31 May 1979)

Periodicity in ion-exchange behaviour of some metal ions in electrolyte media: BINOY K. GHOSH, ASHOK MAHAN and ARUN K. DEY. (31 May 1979)

Determination of traces of silver in copper, lead, zinc, selenium, blister copper, copper-base alloy and lead-base alloy by solvent extraction with tri-n-octylmethylammonium bromide and atomic-absorption spectrometry: IWAO TSUKAHARA and MINORU TANAKA. (1 June 1979)

Determination of dissociation constant and metal–ligand stability constants of tervalent La, Ce, Pr and Sm complexes of 2-mercaptoethanol. R. S. SAXENA and G. L. KHANDELWAL. (1 June 1979)

PMR assay of natural products in pharmaceuticals—III: Assay of griseofulvin: ELSAYED A. ABOUTABL and M. M. A. HASSAN. (1 June 1979)

Linear titration plots with ion-selective electrodes: ARI IVASKA. (4 June 1979)

A new titrant for perchlorate: Cetyltrimethylammonium bromide: WALTER SELIG. (4 June 1979)

Studies on pollutants: Spectrophotometric determination of nitrite as "azoxine dye": ALKA BHATT and V. K. GUPTA. (5 June 1979)

SUBJECT INDEX

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ERRATA

In the paper by K. Ametani, *Talanta*, 1978, **25**, 317, the following corrections should be made.

In Table 1 on p. 318, in column 5 the flow-rate refers to C_2H_2, *not* to C_2H_2/N_2O as printed.

Table 2 on p. 319 should be replaced by the following table, which is also supplied on gummed paper in this issue, for convenience.

Table 2. Comparison of measurements for 50 ppm lead with and without addition of lanthanum chloride

	Sample solution (in 0.1M HCl)			
	No $LaCl_3$		5000 ppm $LaCl_3$	
Foreign element*, *ppm*	obsd., *ppm*	error, (%)	obsd., *ppm*	error, (%)
Y 1000	52.3	+4.6	50.2	+0.4
Eu 2000	52.6	+5.2	51.5	+3.0
Gd 500	52.0	+4.0	50.5	+1.0
Er 2000	51.3	+2.6	50.1	+0.2
Y 1000, Fe 2000, Ga 200	51.1	+2.2	49.8	−0.4
Eu 2000, Fe 2000, Ga 200	51.2	+2.4	50.4	+0.8
Gd 500, Fe 2000, Ga 200	51.4	+2.8	50.5	+1.0
Er 2000, Fe 2000, Ga 200	51.3	+2.6	50.6	+1.2
av.	51.6_5	$+3.3_0$	50.4_5	$+0.9_0$
std. devn.		3.7_0		1.3_8

* Added as chlorides.

In the paper by Å. Olin and B. Wallén, *Talanta*, 1978, **25**, 720, the second paragraph on p. 721 should begin as follows:

Relations for specific cases can quickly be derived from equation (8). Thus for a sample containing only monoprotic acids titrated with base we have $U = 0$, $r = -1$ and all $n_i = m_i = 1$ and obtain the familiar result

$$\left[\sum_{i=1}^{N} U_i/(1 + K_i h)\right] - V = (V + V_0)(h - [OH])/C.K_i = \beta_{i1}$$

$K_i = \beta_{i1}$ is the protonation constant of A_i. It is,...

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PUBLICATIONS RECEIVED

Glassblowing for Laboratory Technicians, 2nd Ed.: R. BARBOUR, Pergamon, Oxford, 1978. Pp. xv + 265. £15 (hard cover), £5 (flexicover).

This copiously illustrated handbook covers all aspects of glass-blowing, and will serve all practitioners of the art from the tyro to the master craftsman. It is full of useful information, ranging from the severely practical on how to perform various operations, to collections of data on the composition and properties of various glasses. Some sections, such as the chapter and appendix on vacuum-line technique, can be read with profit by the research worker. Even the training of glass-blowers is dealt with, and the flexicover edition is well within the financial reach of all. Strongly recommended, and a great bargain.

Annual Reports on Analytical Atomic Spectroscopy, 1977: J. B. DAWSON (ed.), The Chemical Society, London, 1978. Pp. ix + 291. £17.50.

Volume 7 of the Annual Reports maintains the standards set by its predecessors, and sets out in text and tabular form the developments in analytical atomic spectroscopy during 1977. It is divided into two parts, dealing with principles and instrumentation in the first, and applications in the second. Naturally there is some overlap, but that is a benefit for the reader, since there is no need to turn back and forth between widely separated passages to collate information. The inclusion of authors' addresses in the list of references, combined with the author index, will prove a boon not only to those wishing further direct information from the authors concerned, but also any hard-pressed editors trying to find referees for papers.

The Chemical Analysis of Manganese: ROLAND S. YOUNG, The Manganese Centre, Neuilly, 1978. Pp. 32. Free of charge, from The Manganese Centre, 191 Avenue Charles de Gaulle, 92521 Neuilly sur Seine, France.

This little booklet contains clear instructions for the determination of manganese in many materials and by various techniques, and also for analysis of manganese ores for other components.

Literature Survey on Applications of Uniseal® Decomposition Vessels in Chemical Analysis by AAS and Other Instrumental Methods, 1968–1977. Uniseal, Haifa, 1978. Pp. 9. Free of charge from Uniseal Decomposition Vessels Ltd., P.O. Box 9463, Haifa 31094, Israel.

A 9-page fully indexed literature review with over 100 references in some 50 areas of application surveys Uniseal® liquid pressure equipment for the decomposition, solubilization, digestion, extraction, hydrolysis and destruction of organic matter in inorganic and organic materials before application of AAS and other instrumental methods of analysis.

Ion-Selective Electrodes in Organic Elemental and Functional Group Analysis: A Review: W. SELIG, U.S. Department of Commerce, Springfield, VA 22161, 1978. Pp. iv + 127. $7.25. Supplement 1: pp. iv + 57, $5.25.

The review covers the literature abstracted by *Chemical Abstracts* up to the end of Vol. 83 (1975), and the supplement extends the coverage to the end of Vol. 88 (1978). It deals with the determination of the major elements and groups found in organic compounds, and there is a section on the use of ion-selective electrodes as detectors in chromatography. The supplement has an index, but the main review unfortunately does not. However, as most sections are only a few pages in length, the absence of the index is not too serious a drawback.

International Union of Pure and Applied Chemistry, Analytical Chemistry Division, Commission on Microchemical Techniques and Trace Analysis. **General Aspects of Trace Analytical Methods—II. Standard Reference Materials for Trace Analysis: Part 1, Present Status of Availability and Application; Part 2, Available Standard Reference Materials**: O. G. KOCH. **General Aspects of Trace Analytical Methods—III. Contamination in Trace Analysis**: A. MIZUIKE and M. PINTA.

Commission on Electroanalytical Chemistry. **Proposed Terminology and Symbol for the Quantity Representing the Transfer of Solutes from one Solvent to Another**: B. TREMILLON and J. F. COETZEE. **Standard Potential of the Silver–Silver Chloride Electrode**: R. G. BATES and J. B. MACASKILL.

These are all reprints from *Pure and Applied Chemistry*, available from Pergamon Press (prices on application).

coverage deadline during the first 3 months of next year. If this is achieved it will be a spectacular technical achievement. The intention is to issue the whole work in 6 volumes of around 1200 pages each and this article is specifically concerned with Volume 1. My comments on the work as a whole rest therefore on the assumption that Volume 1 is typical of them all; from its layout, its list of contents, and my perusal of the individual chapters this would seem a not unreasonable assumption to make.

I confess that I have been much impressed by Volume 1, largely, of course, because it meets my criteria for a personal reference text for the practising organic chemist. The coverage is on orthodox lines and comprises aliphatic and alicyclic hydrocarbons, arenes, halo-compounds, alcohols, phenols, carbonyl compounds and ethers. It contains the essential factual matter on individual groups of compounds but employs what I would call the Houben–Weyl approach to methods and reactions modernised on the basis of mechanistic ideas and it gives copious and, on the whole, well-chosen references to more detailed sources of information. Volume 1 includes, in addition to chapters on individual compound groups, others on theoretical topics such as stereochemistry and aromaticity which are dealt with in a thoroughly up-to-date manner. On first approaching it I felt the opening chapter on stereochemistry was curiously located, but on further reflection I think that this may be rather unfair. This book is in no sense an introductory text on organic chemistry for undergraduates and to give a comprehensive treatment of modern stereochemistry as a kind of introduction may well be desirable. One criticism which I would make is that the balance is not in my opinion always perfect; for instance I find it hard to believe that quinones warrant no more than 12 pages (and these mainly on benzoquinones) whereas 40 pages are devoted to annulenes. Of course, there are always differences of opinion on the relative importance of individual topics just as there are differences in style of presentation by individual authors, but although there is, here and there, a little unevenness in style, the editors have done such an excellent job in controlling general treatment of topics that any unevenness is not obtrusive. Some other minor criticisms could be made but they would not affect my view that this promises to be a real contribution to the literature of organic chemistry. It is not in competition with the encyclopaedic works of reference which we have but is a comprehensive first source to which the chemist can turn for information and in which he can browse for inspiration. If the other five volumes adequately match the first then *Comprehensive Organic Chemistry* will fill a long-felt need and should be a success.

Reviewed by G. Ourisson, *Strasbourg*:
Volume 2 (Nitrogen Compounds, Carboxylic Acids, Phosphorus Compounds; edited by I. O. Sutherland, *Liverpool*).

The present volume is probably typical of the complete series. It is "medium-sized", has a very wide coverage, relies heavily on existing reviews and books, and is definitely up-to-date.

Its medium size is in line with the British tradition of Rodd's *Chemistry of Carbon Compounds*, and runs opposite to the German ideal of the exhaustive Handbuch, as well as to the American one of the specialised monograph. This intermediate character makes it certainly easier for the reader to scan for the essential points in a domain new to him, at a level deeper than that made accessible by textbooks, and with the provision of key references to the primary literature, and to specialised reviews. In most chapters, the bibliography contains the essential recent books, mentions extensively chemical Reviews or Organic Reactions, Houben–Weyl or Patai, in brief does not make-believe that the author has read all the primary references quoted, and only primary literature. This is of course all to the advantage of the reader, who will certainly want to begin his reading by such reviews. Let us note at this stage that the latest references mentioned are from 1976 to 1977, and that in most chapters, the patent literature is practically ignored. (In this

respect recourse to Houben–Weyl would provide often a completely different picture.)

The coverage is very wide. In this volume of some 1300 pages, eighteen chapters describe classical functions (amines of diverse types, nitriles, esters, etc.), as well as more special ones (e.g. nitrones, nitroxides, phosphazenes . . .). In each case, a classical plan is followed: preparations and reactions are covered in turn, with usually only a very brief mention of the physical properties and of structural aspects. In general, mechanisms are hardly discussed, except when they have a direct bearing on the preparative aspects.

The various chapters are treated in a similar manner, but not at the same level of detail. For instance, the chapter on imines, nitrones, nitriles and isocyanides is exceptionally thorough (nearly 200 pages, 650 references), whereas aromatic amines, to which certainly much more work has been devoted, are covered in 50 pages, with some 200 references. In fact, I believe this is probably once again favourable for the reader, who gets most of what he needs most: help with the less accessible information.

It is extremely difficult to gauge such a large book by scanning it or by reading parts of it; it is also certainly not meant to be read through. An impression can however be gained easily in the few hours I have spent probing, reading, comparing. It is definitely very favourable. I am convinced that the emphasis is right; that the book, and certainly the series, will find daily use in most organic chemical laboratories, for quite a long time. Of course, it will be most useful only to those who have access to a well-stocked library, but it must be pointed out that, even from that point of view, the reader has been favoured; at least the Anglo-Saxon reader, as the bulk of the references are to American and British articles, with only occassional intrusion of German (few), Japanese (very few), Swiss, Russian or French papers (rare).

Reviewed by G. Stork, *New York*:
Volume 3 (Sulphur, Selenium, Silicon, Boron, Organometallic Compounds; edited by D. Neville Jones, *Sheffield*).

This volume starts with the organic chemistry of sulfur, from thiols to thiocarbonyl compounds, via sulfinylamines and thiosulfonates, which it covers in some 480 pages with almost 2000 references. This is followed by organoselenium and tellurium compounds (46 pages, 279 references), organic compounds of silicon (145 pages, 633 references), and of boron (251 pages, 842 references). We then encounter organometallic compounds of groups I, II, III and IV, and of antimony and bismuth (175 pages, 777 references). The volume closes with organic compounds of the transition metals (196 pages, 179 references). This is a breath-taking accomplishment for many reasons.

The sixteen writers of Volume 3 are not only possessed of what appears to be an encyclopaedic knowledge of their subject. They are, without exception, deeply involved in research in the field they cover and are, indeed, immediately recognized as among the foremost contributors to its recent developments. That such a galaxy of authors could be assembled, that it could bring such a project to fruition on schedule, that it could maintain some unity of presentation and a largely successful concern for relevance to synthetic organic chemists, is an extraordinary achievement. The Chairman of the Editorial Board, Professor D. H. R. Barton, his Deputy, Professor W. D. Ollis, as well as the Editor of this particular volume, Dr. D. N. Jones, have our admiration and deserve our thanks.

Judging by this volume, which I take to be representative of the whole work, it is clear that every serious chemistry library will have to acquire this set.

This being said, I will now comment more specifically on the material in Volume 3 if only to show that my recommendation is based on actual reading of this volume. I will start with some minor criticism. The book is completely oriented toward leading the practising chemist to recent, operationally useful, literature references on a particular reaction. In this it has succeeded, and this is obviously a major strength, but a corollary is that this is not a book which can be consulted to get a sense of the history or intellectual

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Pergamon Press Ltd., 1979. Printed in Great Britain

PUBLICATIONS RECEIVED

Laboratory Handbook of Chromatographic and Allied Methods: edited by O. MIKEŠ, Horwood, Chichester, 1979. Pp. 764. £38.50.

In the reviewer's opinion there are too many books on chromatography and related methods. An earlier book edited by Mikeš had numerous competitors. Each book should justify its existence. This new one does. It is not a second edition of the previous manual but a refreshingly modern book which within its wide range deals clearly and in reasonable depth with equipment and materials readily available in the West. The book describes not only the principles involved but gives examples of applications and how to select and improve methods. Chromatography is still partly an art, or skill, and a particularly attractive feature of this book is that the experience of the contributors is revealed in the way they deal with minor handling techniques, and with other, at first sight apparently trivial, matters all of which in fact largely determine whether or not a chromatographic method will be found to be successful. The book is large and for many users should be on its own self-sufficient, but it is impossible, and in this field impractical and undesirable, for any text to seek to be comprehensive. Reference is made to specialist texts.

The topics covered include theories of chromatographic and related methods, applications of partition, adsorption, ion-exchange, gel, affinity and gas chromatography and techniques of column, paper, thin-layer and other types of chromatography. There are chapters on electromigration and countercurrent distribution, and the book ends with a useful review of the literature and a list of United Kingdom suppliers of materials and equipment. The chapters vary in style and scope but overall the coverage is good. In such a large book it is not surprising that there are a few outdated terms and typographical errors. The historical introductions are interesting and well-balanced. The book is indeed what its predecessor claimed to be, namely a laboratory, or bench, manual and in that appropriate guise it will prove of considerable value for reference and browsing. It is an excellent guide through the jungle of competing techniques, chromatographic reagents and suppliers, and will be of some help in assisting in decisions about the most suitable commercially available equipment. Both the novice, and the already experienced worker, will benefit from the expertise displayed.

K. C. B. WILKIE

Modern Methods for Trace Element Analysis: M. PINTA, Ann Arbor Science, Ann Arbor, Michigan, 1978. Pp. xii + 492. £18.60.

This text offers a useful introduction to the application of some selected analytical techniques to trace element analysis. The techniques included are fluorimetry, emission spectroscopy, atomic-absorption spectrometry, atomic-fluorescence spectrometry, X-ray fluorescence spectrometry and activation analysis. For each topic, the theory is discussed briefly, then the apparatus and operational procedures are discussed, and finally a wide selection of practical methods is given. References to the original literature are extensive. The chapters on atomic-absorption methods, which include extensive discussion of non-flame methods, will be particularly useful to the newcomer to modern routine trace analytical practice. In his introduction, the author tries to justify the omission of several important modern techniques, including electrochemical stripping methods, differential-pulse polarography, ion-selective electrodes, and spark-source mass spectrometry: it would have been preferable if he had merely stated that he did not propose to discuss them.

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MARY MASSON

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The cost per page is comparatively high, especially in view of the poor paper and printing. It is, however, a useful compilation for anyone wishing to devise or modify a method and on that basis the price is by no means outrageous. The text is clearly written and well illustrated and the book's merits far outweigh any defects I have pointed out.

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DEREK MIDGLEY

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FOREWORD

The Editorial Board and Publisher of *Talanta* take great pleasure in presenting this special issue as a tribute to the many and varied contributions to the analytical sciences made by chemists in Germany, from earliest times to the present. They consider it appropriate to link the issue with the name of CARL FRIEDRICH MOHR, in the year of the 100th anniversary of his death. Except for the biographical sketch and a few papers specially invited from neighbouring German-speaking countries, all the contributions to this issue originate from current analytical research in Germany, and give a picture of the breadth and scope of modern interests in analysis.

The contributions to the issue have not been grouped in any special order of subject matter, since they fall into many different parts of the spectrum of modern analytical chemistry, ranging from the simplicity of classical methods to the complexities of modern instrumentation and the demands of technology. Taken overall, they represent a very good cross-section of current interests in analytical research in Germany and show well the close relationship between pure and applied research that has always existed to a far greater extent in analysis than in other branches of chemistry. The papers presented here also demonstrate clearly that there is indeed a resurgence in analytical chemistry, as Professor Belcher said in his Plenary Lecture at the 4th International SAC conference in Birmingham in 1977. It is to be hoped that they will be read by the rising generation of students and analysts and help to arouse that interest and enthusiasm so necessary for the successful practice of the analyst's craft.

E. Blasius
R. A. Chalmers

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NOTICES

GORDON RESEARCH CONFERENCES
New Hampshire

The 1979 Gordon Research Conferences of major interest to analytical chemists include the following:

Chemistry at Interfaces, 2–6 July, Kimball Union Academy, Meriden
Analytical Pyrolysis, 2–6 July, Holderness School, Plymouth
Quantitative Structure Analysis, 16–20 July, Plymouth State College, Plymouth
Point and Line Defects in Semiconductors, 23–27 July, Kimball Union Academy
Statistics in Chemistry and Chemical Engineering, 30 July–3 August, New Hampton School, New Hampton
Toxicology and Safety Evaluations, 30 July–3 August, Kimball Union Academy
Micellar and Macromolecular Catalysis, 6–10 August, Brewster Academy, Wolfeboro
Separation and Purification, 13–17 August, Colby-Sawyer College, New London
Analytical Chemistry, 13–17 August, New Hampton School
Fluids in Permeable Media, 13–17 August, Kimball Union Academy
Laser Interaction with Matter, 13–17 August, Tilton School, Tilton
Chemistry and Physics of Liquids, 13–17 August, Holderness School
Ion Exchange, 20–24 August, Kimball Union Academy
Elementary Particle Interactions, 20–24 August, Proctor Academy, Andover
Inorganic Geochemistry, 20–24 August, Holderness School
Molten Salts and Metals, 20–24 August, Brewster Academy
Remote Sensing of the Earth's Surface from Space, 20–24 August, Plymouth State College

Full information available from:

Dr. A. M. Cruickshank, Director,
Gordon Research Conferences,
Pastore Chemical Laboratory,
University of Rhode Island,
Kingston, Rhode Island 02881, U.S.A.

ISEC '80
International Solvent Extraction Conference 1980
Liège, Belgium, 6–12 September 1980

The intended audience of the conference is one of chemists and chemical engineers from industry, universities and research centers who are concerned with all practical or fundamental aspects of solvent extraction. As in the past, the conference will be devoted to topics such as chemistry and physical chemistry of extraction, extraction equipment, industrial processes and economics, nuclear chemistry, application to petrochemical and pharmaceutical industries.

ISEC 80 will take place at the University of Liège on the new Sart-Tilman Campus. The University provides the convenience of modern conference rooms and of libraries in a woodland setting. The accommodation for delegates will be offered either on the Sart-Tilman Campus or in town.

The scientific programme will include invited plenary lectures and submitted research papers. Specialized papers will be presented in poster sessions in order to encourage direct contacts between those most interested. Poster sessions proved to be a real success at the ISEC conference in Toronto.

A sightseeing tour is planned on Sunday, September 7th and technical tours to Belgian and nearby German plants and laboratories are planned on Wednesday, September 10th.

The proceedings will be published by a photographic reduction process in advance of the conference and will be distributed to participants on registration at the University of Liège. The language of the conference will be English.

Authors are invited to submit by July 1st, 1979 an extended abstract (minimum 600 words plus figures). The papers should present original unpublished research works and will be submitted to referees. Authors will be notified of the provisional acceptance or of the rejection of their contributions in autumn 1979.

Manuscript of the full papers will be due by February 1st, 1980.

Conference secretariat:
ISEC 80, Department of Chemistry, University of Liège, Sart-Tilman, B 4000, Liège, Belgium.

STANDARD REFERENCE SAMPLES OF METALLURGICAL DUSTS FOR ENVIRONMENTAL CONTROL ANALYSIS

In view of existing and probable future legislation regarding the emission of particulate matter into the atmosphere, and the high capital cost of meeting these requirements, there is a growing interest in the composition of such dusts which are recovered for either re-use or disposal.

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PUBLICATIONS RECEIVED

Analysis of Drugs and Metabolites by Gas Chromatography–Mass Spectrometry, Volume 5: B. J. GUDZINOWICZ and M. J. GUDZINOWICZ, Dekker, New York, 1978. Pp. x + 541. S.Fr. 140.00.

This latest volume of the exhaustive treatise dealing with medical applications of the combined gas chromatograph–mass spectrometric technique is devoted to the analysis of analgesics, local anaesthetics and antibiotics. After a brief philosophical introduction outlining the application of narcotics to the relief of pain, there follows a review of the methods which have been proposed for the assay and identification of pain-relieving drugs. This material is grouped under the headings of naturally-occurring opium alkaloids and their derivatives, synthetic opium-like drugs and narcotic antagonists. Succeeding sections describe work on the analysis of other substances used in pain relief, such as the antipyretic and anti-inflammatory drugs. The remaining text is concerned with methods for local anaesthetics and antibiotics. Full experimental details are often provided and techniques involving newer methods of ionization are not neglected. There are also included tables of pharmacokinetic data for some of the substances described.

J. R. MAJER

The Study of Ionic Equilibria: An Introduction: HAZEL ROSSOTTI, Longmans, London, 1978. Pp. xiv + 194. £5.95.

This is a readable and readily understandable account of the methods of determining acid-base and metal-ion equilibrium constants. It was written for senior undergraduate students, but it will be equally useful to postgraduate students and to others who wish to determine stability constants, but did not have the benefit of being taught by an enthusiast like Dr. Rossotti.

After two brief introductory chapters, the "meat" of the book begins with a discussion of the protonation of monoprotic acids. The treatment is done in terms of both dissociation constants and formation constants. Both are clearly defined, as is the relationship between them. The various species of constants—activity quotients, concentration quotients, and mixed "Brønsted" constants—are defined, and their usefulness in theory and practice is discussed. Methods for studying equilibria are then described: the advantages and disadvantages of potentiometry, spectrophotometry, distribution methods, and conductivity measurements are compared and contrasted. Step by step, the discussion is extended to two-stage protonations, several-stage protonations, and the binding of protons to macromolecules.

A similar pattern is followed for metal-ion complexes, except that formation constants only are used. The algebra is first presented for the formation of a simple complex where no side-reactions are involved. Later, the idea of competition with protons is introduced. Again, the appropriate experimental methods are discussed, with just the right amount of detail for a treatment at this level. The treatment is extended to ternary and polynuclear complexes in the final part of this section.

In a critical treatment of computational methods, the graphical and computerized approaches are described in detail, and their advantages and disadvantages are discussed. The final chapter attempts to show *why* equilibrium constants are determined: it covers calculation of equilibrium concentrations, graphical display of results for systems of widely varying complexity, and evaluation of other parameters (including correlation studies).

I can strongly recommend this book to anyone who is interested in determining equilibrium constants, and especially anyone who has found the "tough generalized treatment of acids and metal complexes" (which is how the bibliography describes *The Determination of Stability Constants*, by F. J. C. Rossotti and H. S. Rossotti) just too tough for comfort.

MARY MASSON

Topics in Bioelectrochemistry and Bioenergetics Volume 2: G. Milazzo (ed.), Wiley, New York, 1978. Pp. 204. £13.00.

This book consists of six chapters in the form of monographs, each by different authors. The subjects covered are (1) Mechanisms of Membrane Excitability, (2) Electrokinetic Phenomena in Biology, (3) A Potential Controlled Transient Gating Mechanism in Fixed Charge Membrane Modules, (4) Analytical Electrophoresis, (5) Electrical Events During Active Transport of Ions through Biological Membranes, and (6) Semiconducting Biopolymers and their part in Biochemical Phenomena. The chapters are mainly of a review nature but some original material is also included. In the preface to the series, the editor writes that the chapters are written "at a high level, by authoritative electrochemists for the particular benefit of biochemists and biologists, and by authoritative biochemists and biologists for the particular benefit of electrochemists", and on the whole this pedagogical aim has been achieved. For those new to the subject, the chapters may not make easy reading, but they are clearly and concisely written and the bibliography is extensive enough to enable the reader to follow up any points on which he may need further clarification. The detailed derivations of some of the equations are given in appendices. Although the authors come from many different countries, all the chapters are in English with a consistently clear style. The general presentation and printing of the book is also to a high standard. It seems strange that the only reference to Volume 1 of the series is on the dust cover.

PETER H. LLOYD

Blood Drugs and Other Analytical Challenges: ERIC REID (ed.) Horwood, Chichester, 1978. Pp. 355. £19.50.

This book reports the deliberations of a Bioanalytical Forum held at the Wolfson Centre of the University of Surrey in September 1977. It is the 7th in the series "Methodological Surveys in Biochemistry" and is closely related to

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This book consists of six chapters in the form of monographs, each by different authors. The subjects covered are (1) Mechanisms of Membrane Excitability, (2) Electrokinetic Phenomena in Biology, (3) A Potential Controlled Transient Gating Mechanism in Fixed Charge Membrane Modules, (4) Analytical Electrophoresis, (5) Electrical Events During Active Transport of Ions through Biological Membranes, and (6) Semiconducting Biopolymers and their part in Biochemical Phenomena. The chapters are mainly of a review nature but some original material is also included. In the preface to the series, the editor writes that the chapters are written "at a high level, by authoritative electrochemists for the particular benefit of biochemists and biologists, and by authoritative biochemists and biologists for the particular benefit of electrochemists", and on the whole this pedagogical aim has been achieved. For those new to the subject, the chapters may not make easy reading, but they are clearly and concisely written and the bibliography is extensive enough to enable the reader to follow up any points on which he may need further clarification. The detailed derivations of some of the equations are given in appendices. Although the authors come from many different countries, all the chapters are in English with a consistently clear style. The general presentation and printing of the book is also to a high standard. It seems strange that the only reference to Volume 1 of the series is on the dust cover.

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After two brief introductory chapters, the "meat" of the book begins with a discussion of the protonation of monoprotic acids. The treatment is done in terms of both dissociation constants and formation constants. Both are clearly defined, as is the relationship between them. The various species of constants—activity quotients, concentration quotients, and mixed "Brønsted" constants—are defined, and their usefulness in theory and practice is discussed. Methods for studying equilibria are then described: the advantages and disadvantages of potentiometry, spectrophotometry, distribution methods, and conductivity measurements are compared and contrasted. Step by step, the discussion is extended to two-stage protonations, several-stage protonations, and the binding of protons to macromolecules.

A similar pattern is followed for metal-ion complexes, except that formation constants only are used. The algebra is first presented for the formation of a simple complex where no side-reactions are involved. Later, the idea of competition with protons is introduced. Again, the appropriate experimental methods are discussed, with just the right amount of detail for a treatment at this level. The treatment is extended to ternary and polynuclear complexes in the final part of this section.

In a critical treatment of computational methods, the graphical and computerized approaches are described in detail, and their advantages and disadvantages are discussed. The final chapter attempts to show *why* equilibrium constants are determined: it covers calculation of equilibrium concentrations, graphical display of results for systems of widely varying complexity, and evaluation of other parameters (including correlation studies).

I can strongly recommend this book to anyone who is interested in determining equilibrium constants, and especially anyone who has found the "tough generalized treatment of acids and metal complexes" (which is how the bibliography describes *The Determination of Stability Constants*, by F. J. C. Rossotti and H. S. Rossotti) just too tough for comfort.

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NOTICE

FEDERATION OF EUROPEAN CHEMICAL SOCIETIES (FECS)

WORKING PARTY ON ANALYTICAL CHEMISTRY (WPAC)

European Analytical Column 2

As in 1978, when this European Analytical Column first appeared in all major European broad-spectrum journals of Analytical Chemistry and outlets of the national member societies, the WPAC/FECS wishes to inform the analytical community about recent activities.

In 1978, two meetings (Nos. 8 and 9) of the WPAC took place in Dublin, Ireland, on the occasion of the Euroanalysis III conference. Professor H. Malissa, was re-elected as chairman for a further period of 3 years. After the nomination of a Spanish representative the WPAC now has 29 members representing 25 national societies of 19 European countries.

At the Dublin meetings the following items were discussed.

(i) *Euroanalysis III* (20–25 August 1978, Dublin). This latest of the European broad-spectrum conferences on Analytical Chemistry was again a very successful event and was attended by more than 700 delegates from 38 countries. The scientific programme consisted of 5 plenary, 11 keynote and 180 contributed papers and 150 posters. In addition, special sessions on Reference Materials and on Education in Analytical Chemistry were of great interest to the participants and provided an excellent survey of these fields in Europe. The contributions to the special session on Education will be published in Zeitschrift für Analytische Chemie: the plenary and the keynote lectures will appear as Proceedings of the Conference (editor D. M. Carroll; publisher Applied Science, London).

(2) Reflections on the influence of the copyright laws on the freedom and speed of publication are under way.

(3) *Euroanalysis IV* (23–28 August 1981, Helsinki). The next Euroanalysis conference will again be organized as a broad spectrum conference, including the treatment of selected topics in special sessions, such as "Extraction of Information in Analytical Chemistry", "Analytical Chemistry, legislation, execution and responsibility" or other topics and a joint special session with IUPAC on "Harmonization of collaborative analytical studies". It was further decided to organize the *Euroanalysis V* conference (1984) in Cracow.

(4) *FECHEM-conference on Computer-Based Analytical Chemistry* (COBAC), 20th event of the FECS, Portorož, 24–28 September 1979. Organizer: Professor D. Hadži, Ljubljana. This conference will start a new series that should treat the pertinent problems which were hitherto dispersed amonst various more general meetings. The scope of the COBAC meetings is rather large and includes all aspects of computerization of analytical work, *i.e.*, from mathematical and statistical fundamentals to practical solutions of particular analytical tasks, wherever computer-based philosophy and technology enter the scene.

(5) *FECHEM-conference on Education in Analytical Chemistry*, 21st event of the FECS, Vienna, 10–22 December 1979.
Organizer: Professor H. Malissa, Vienna.
Scientific committee:

H. Malissa, Austria (Chairman)
D. Betteridge, UK
D. Burns, N. Ireland
W. Fresenius, FRG
G. den Boef, Netherlands
E. Pungor, Hungary
I. Garaj, CSSR
Y. Zolotov, USSR
R. Kellner, Austria (Secretary)

Based on the experiences of the special session in Dublin (1978) and the evaluation of the papers and posters presented on that topic, this conference will provide a unique and important possibility to create a new picture of education in modern Analytical Chemistry at university level.

Main emphasis will be given to "Scope and didactic aspects of computers in teaching of Analytical Chemistry" in plenary lectures and small group discussions.

(6) *Joint venture between WPAC and the Analytical Division of IUPAC.* A joint study group was established in order to study the possibilities for solving the problems connected with the increasing literature in Analytical Chemistry (*e.g.*, use of symbolic language). The members are:

WPAC: Cserfalvi, Griepink, Kelker, Malissa, Simeonov
Editors: Fresenius, Macdonald
IUPAC: to be announced

(7) It was decided to continue the discussion on *Feasibility of standard reference materials* (*SRM*). Experts in new fields of Analytical Chemistry are invited to present their opinions. Professor R. Belcher, Birmingham, will act as co-ordinator.

(8) Colleagues who are interested in further details are kindly requested to contact the secretary of the WPAC:

Prof. R. Kellner
Institut für Analytische Chemie und Mikrochemie
Technische Univerversität Wien
Getreidemarkt 9
A-1060 Wien/Austria

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NOTICES

GORDON RESEARCH CONFERENCES
New Hampshire

The 1979 Gordon Research Conferences of major interest to analytical chemists include the following:

Chemistry at Interfaces, 2–6 July, Kimball Union Academy, Meriden
Analytical Pyrolysis, 2–6 July, Holderness School, Plymouth
Quantitative Structure Analysis, 16–20 July, Plymouth State College, Plymouth
Point and Line Defects in Semiconductors, 23–27 July, Kimball Union Academy
Statistics in Chemistry and Chemical Engineering, 30 July–3 August, New Hampton School, New Hampton
Toxicology and Safety Evaluations, 30 July–3 August, Kimball Union Academy
Micellar and Macromolecular Catalysis, 6–10 August, Brewster Academy, Wolfeboro
Separation and Purification, 13–17 August, Colby-Sawyer College, New London
Analytical Chemistry, 13–17 August, New Hampton School
Fluids in Permeable Media, 13–17 August, Kimball Union Academy
Laser Interaction with Matter, 13–17 August, Tilton School, Tilton
Chemistry and Physics of Liquids, 13–17 August, Holderness School
Ion Exchange, 20–24 August, Kimball Union Academy
Elementary Particle Interactions, 20–24 August, Proctor Academy, Andover
Inorganic Geochemistry, 20–24 August, Holderness School
Molten Salts and Metals, 20–24 August, Brewster Academy
Remote Sensing of the Earth's Surface from Space, 20–24 August, Plymouth State College

Full information available from:

Dr. A. M. Cruickshank, Director,
Gordon Research Conferences,
Pastore Chemical Laboratory,
University of Rhode Island,
Kingston, Rhode Island 02881, U.S.A.

ISEC '80
International Solvent Extraction Conference 1980
Liège, Belgium, 6–12 September 1980

The intended audience of the conference is one of chemists and chemical engineers from industry, universities and research centers who are concerned with all practical or fundamental aspects of solvent extraction. As in the past, the conference will be devoted to topics such as chemistry and physical chemistry of extraction, extraction equipment, industrial processes and economics, nuclear chemistry, application to petrochemical and pharmaceutical industries.

ISEC 80 will take place at the University of Liège on the new Sart-Tilman Campus. The University provides the convenience of modern conference rooms and of libraries in a woodland setting. The accommodation for delegates will be offered either on the Sart-Tilman Campus or in town.

The scientific programme will include invited plenary lectures and submitted research papers. Specialized papers will be presented in poster sessions in order to encourage direct contacts between those most interested. Poster sessions proved to be a real success at the ISEC conference in Toronto.

A sightseeing tour is planned on Sunday, September 7th and technical tours to Belgian and nearby German plants and laboratories are planned on Wednesday, September 10th.

The proceedings will be published by a photographic reduction process in advance of the conference and will be distributed to participants on registration at the University of Liège. The language of the conference will be English.

Authors are invited to submit by July 1st, 1979 an extended abstract (minimum 600 words plus figures). The papers should present original unpublished research works and will be submitted to referees. Authors will be notified of the provisional acceptance or of the rejection of their contributions in autumn 1979.

Manuscript of the full papers will be due by February 1st, 1980.

Conference secretariat:
ISEC 80, Department of Chemistry, University of Liège, Sart-Tilman, B 4000, Liège, Belgium.

STANDARD REFERENCE SAMPLES OF METALLURGICAL DUSTS FOR ENVIRONMENTAL CONTROL ANALYSIS

In view of existing and probable future legislation regarding the emission of particulate matter into the atmosphere, and the high capital cost of meeting these requirements, there is a growing interest in the composition of such dusts which are recovered for either re-use or disposal.

The control of the chemical composition of metallurgical dusts is, therefore, an important part of the work of steelworks laboratories. To assist them in the control of the analysis of these dusts and for the calibration of physical analytical instruments, the following Standard Samples have been prepared and certified under the auspices of the European Coal and Steel Community:

ES. 876-1 Electric Furnace Dust prepared by IRSID in France,

ES. 877-1 LD Converter Dust prepared by BAS in the UK.

Each sample has been analysed by approximately 20 European Laboratories and specimens of the Certificates of Analyses are supplied with each sample.

It is expected that these dust standards will also be of interest to many laboratories looking for reference materials for environmental control analysis in other industries.

Supplies of both samples are available in the UK from Bureau of Analysed Samples Limited, Newham Hall, Newby, Middlesbrough.

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Volume 5 of the same series. In his preface Dr. Reid points out "It may encourage journal referees to press authors for methodological *rationale* rather than recipes", and the book itself lives up to this standard. In early chapters emphasis is placed on the importance of Quality Control and Sources of Error (Scales), and of the value of Internal Standardization (Curry and Whelpton). The chapter on Glass Capillary GC by Grob is profoundly workmanlike, and it is refreshing to meet such down-to-earth subheadings as 'Dirt in parts of the GC assembly'. Schill contributes a useful chapter on Ion-pair HPLC, and Kissinger's observations on Reverse Phase HPLC with Amperometric Detection reminded the reviewer of long forgotten electrochemistry. Scattered throughout the text are interesting case histories including one on the TCDD incident at Seveso. The book concludes with a useful Index of Compound Types which back references also to Volume 5. Apart from a very few typographical errors the only criticism which might be offered is that it would have been preferable to have the "Comments and Dialogue" appended to each chapter rather than to isolate these at the end of the book. This is essentially a "tips" book, and as such should be in any departmental library where this kind of analytical work is done. For its content the cost is not high.

W. B. YEOMAN

GLC and HPLC Determination of Therapeutic Agents, Part 1: K. TSUJI and W. MOROZOWICH (eds.), Dekker, New York, 1978. Pp. xiv + 415. S.Fr. 98.00.

This is the first part of a three-volume work devoted to analysis by gas and liquid chromatography. The three parts together will constitute Volume 9 of the series describing various aspects of chromatography. The text is arranged in thirteen chapters, written by no less than twenty-two authors, each chapter being concerned with some particular facet of the application of the twin techniques to the assay of therapeutic substances. Much of this material has been reviewed before, both in the literature and in numerous books. This applies particularly to the chapters dealing with the theory of gas chromatography, the properties of stationary phases and the coupling of mass spectrometers with gas chromatographs. Less familiar will be those sections outlining the use of derivatives in HPLC and the application of the mass spectrometer as a detector in HPLC. In the latter case the technology in this particular form of instrumentation is advancing at a rapid rate and the inclusion of the most recent developments is welcome. Other topics reviewed in detail in succeeding chapters are the scaling-up of chromatographic methods for preparative purposes, the automation of chromatographic systems and the use of computers for processing chromatographic data. This will be a useful book for the practising analytical chemist, bringing together as it does information on the two complementary chromatographic techniques and providing a valuable survey of sample pre-treatment methods.

J. R. MAJER

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TALANTA ADVISORY BOARD

The Editorial Board and Publishers of *Talanta* take pleasure in welcoming the following new members to the Advisory Board of the journal.

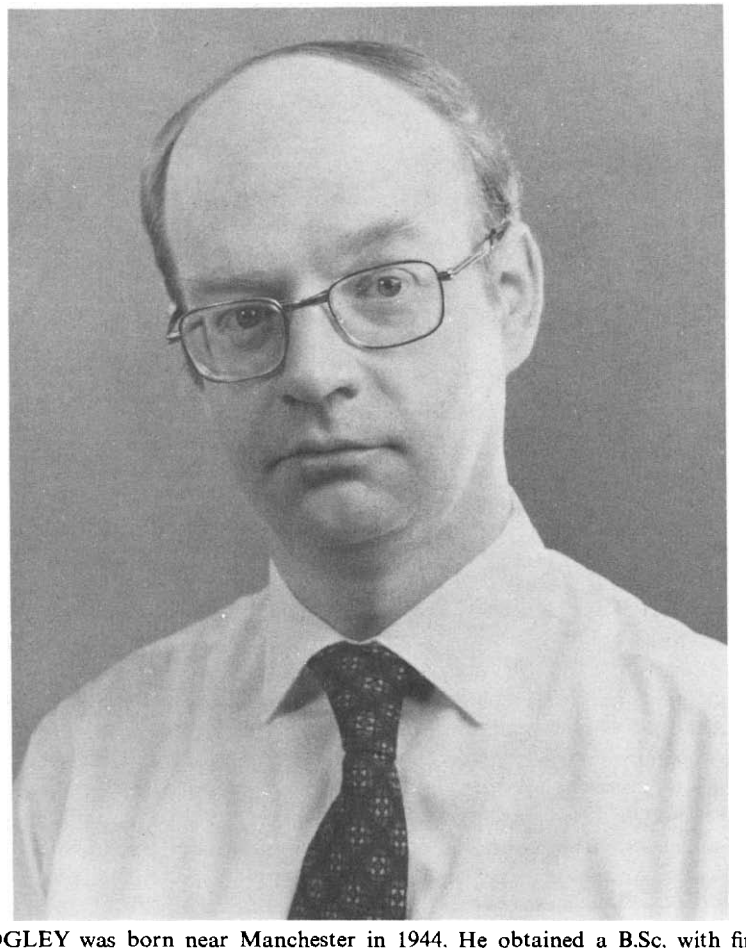
D. MIDGLEY
M. THOMPSON

They also with to record their sincere thanks for the help given by

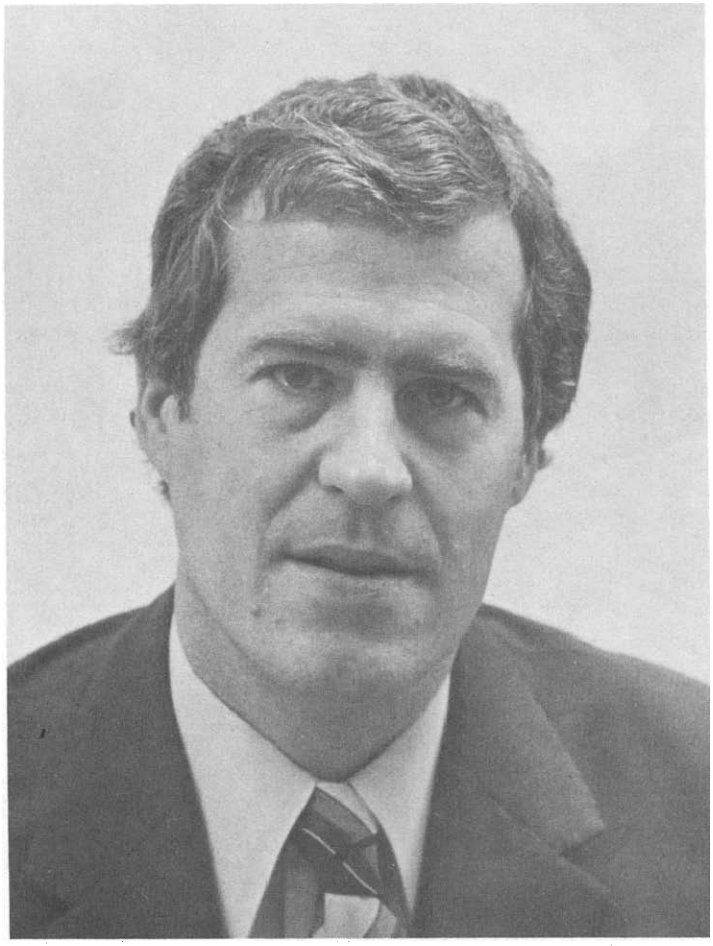
H. FLASCHKA
J. K. FOREMAN

who retire from the Advisory Board.

They also wish to record their sincere thanks and appreciation to Dr. R. PŘIBIL who has been a Regional Editor of *Talanta* since its inception, but who has now retired and so will relinquish his editorship and join the Advisory Board instead. The new Regional Editor will be Professor E. PUNGOR, who has served on the Advisory Board for a number of years.



DR. DEREK MIDGLEY was born near Manchester in 1944. He obtained a B.Sc. with first class honours in chemistry at the University of Glasgow in 1966 and a Ph.D. from the same university for research on the thermodynamics of complexing in electrolyte solutions. In 1970 he joined the Central Electricity Generating Board to work in the Analytical Chemistry Section of the Central Electricity Research Laboratories in Leatherhead. His research at C.E.R.L. has been mainly concerned with the use of ion-selective electrodes for the analysis of high-purity waters. This has involved working near the limits of capability of electrodes and has led to an interest in the problems of limits of detection. Another of his interests is the theory of potentiometric titrations and the application of computing methods to titrimetry. He is co-author of a book "Potentiometric Water Analysis" and has published some three dozen papers.



PROFESSOR M. THOMPSON started his career in traditional fashion for British analysts, as a laboratory assistant (in his case with the British Steel Corporation), and by part-time study obtained his Ordinary and Higher National Certificates in chemistry before going on to obtain an honours degree in Chemistry at University College of Swansea, followed by a Ph.D. from McMaster University in Canada and an F.R.I.C. He has been a Post-Doctoral Fellow at Swansea, lecturer at Loughborough University, and successively Assistant Professor and now Associate Professor of Analytical Chemistry at the University of Toronto. He is very active in various chemical societies, and his research interests lie in the fields of ultraviolet and X-ray photoelectron spectroscopy, Auger emission spectroscopy, design of molecular separators for gas chromatography/mass spectrometry, chemoreceptor membranes in trace organic analysis, and use of coated electronic devices in selective organic analysis.

respect recourse to Houben–Weyl would provide often a completely different picture.)

The coverage is very wide. In this volume of some 1300 pages, eighteen chapters describe classical functions (amines of diverse types, nitriles, esters, etc.), as well as more special ones (e.g. nitrones, nitroxides, phosphazenes . . .). In each case, a classical plan is followed: preparations and reactions are covered in turn, with usually only a very brief mention of the physical properties and of structural aspects. In general, mechanisms are hardly discussed, except when they have a direct bearing on the preparative aspects.

The various chapters are treated in a similar manner, but not at the same level of detail. For instance, the chapter on imines, nitrones, nitriles and isocyanides is exceptionally thorough (nearly 200 pages, 650 references), whereas aromatic amines, to which certainly much more work has been devoted, are covered in 50 pages, with some 200 references. In fact, I believe this is probably once again favourable for the reader, who gets most of what he needs most: help with the less accessible information.

It is extremely difficult to gauge such a large book by scanning it or by reading parts of it; it is also certainly not meant to be read through. An impression can however be gained easily in the few hours I have spent probing, reading, comparing. It is definitely very favourable. I am convinced that the emphasis is right; that the book, and certainly the series, will find daily use in most organic chemical laboratories, for quite a long time. Of course, it will be most useful only to those who have access to a well-stocked library, but it must be pointed out that, even from that point of view, the reader has been favoured; at least the Anglo-Saxon reader, as the bulk of the references are to American and British articles, with only occassional intrusion of German (few), Japanese (very few), Swiss, Russian or French papers (rare).

Reviewed by G. Stork, *New York*:
Volume 3 (Sulphur, Selenium, Silicon, Boron, Organometallic Compounds; edited by D. Neville Jones, *Sheffield*).

This volume starts with the organic chemistry of sulfur, from thiols to thiocarbonyl compounds, via sulfinylamines and thiosulfonates, which it covers in some 480 pages with almost 2000 references. This is followed by organoselenium and tellurium compounds (46 pages, 279 references), organic compounds of silicon (145 pages, 633 references), and of boron (251 pages, 842 references). We then encounter organometallic compounds of groups I, II, III and IV, and of antimony and bismuth (175 pages, 777 references). The volume closes with organic compounds of the transition metals (196 pages, 179 references). This is a breath-taking accomplishment for many reasons.

The sixteen writers of Volume 3 are not only possessed of what appears to be an encyclopaedic knowledge of their subject. They are, without exception, deeply involved in research in the field they cover and are, indeed, immediately recognized as among the foremost contributors to its recent developments. That such a galaxy of authors could be assembled, that it could bring such a project to fruition on schedule, that it could maintain some unity of presentation and a largely successful concern for relevance to synthetic organic chemists, is an extraordinary achievement. The Chairman of the Editorial Board, Professor D. H. R. Barton, his Deputy, Professor W. D. Ollis, as well as the Editor of this particular volume, Dr. D. N. Jones, have our admiration and deserve our thanks.

Judging by this volume, which I take to be representative of the whole work, it is clear that every serious chemistry library will have to acquire this set.

This being said, I will now comment more specifically on the material in Volume 3 if only to show that my recommendation is based on actual reading of this volume. I will start with some minor criticism. The book is completely oriented toward leading the practising chemist to recent, operationally useful, literature references on a particular reaction. In this it has succeeded, and this is obviously a major strength, but a corollary is that this is not a book which can be consulted to get a sense of the history or intellectual

background of a method. To give but three examples, the rearrangement of penicillin sulfoxide to cephalosporins is discussed without mention of the seminal work of Morin and the Lilly Laboratories; the alkylation of carbanions to thiolsulfonates is discussed with no references to Smiles; the contribution of Tsuji in the use of palladium complexes to form carbon–carbon bonds is mentioned, but there is no suggestion of its pioneering nature. This is not so much a criticism as a reminder to the users of the book.

The book is not especially concerned with mechanism and its usefulness is, therefore, not really affected by the (very few) questionable statements one inevitably encounters, such as comments on the addition of benzoylsulfene (p. 419), on the reason for the formation of allylic alcohols from selenoxides (compare p. 494 with p. 501), on what is, perhaps unfortunately, termed 1,3-additions to carbonyl compounds (p. 981), on the nature of Zn enolates (p. 992). *Misleading* statements are, as one would expect, extremely rare, one such concerning the suggested generality of the addition of Grignard reagents to imines.

There are some surprising omissions, inter alia, no explicit mention of the opening of epoxides with ethynyl alanes, the reduction of nitriles to aldehydes with diisobutylaluminum hydride, the use of β-heterosubstituted lithium and magnesium reagents, the conjugate reduction of α,β-unsaturated carbonyl compounds with tin hydrides, oxidative and protic destannylation. Some qualitative mechanistic statements would sometimes have helped, e.g. formation of aziridines from oximes (p. 978). On the other hand, the rather esoteric and somewhat limited opening of epoxides with $HCo(CO)_4$ is mentioned twice with equations (p. 1149 and 1236).

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Solvent Extraction in Flame Spectroscopic Analysis: M. S. CRESSER, Butterworths, London, 1978. Pp. x + 200. £15.00.

As one would be entitled to expect of a monograph of only 200 pages costing as much as this one, the book is well produced and proof-read, pleasant to handle and to read.

In content I found it disappointing; the author has set out to produce "an introduction with a strong practical bias", yet only 61 pages of the 200 are on applications. Of the remainder, there are a total of 50 pages listing over 1000 references, 795 of which refer to applications. The remaining pages are devoted to the theory of AAS, AFS and AES, the theory of solvent extraction and one good chapter on the practicalities of solvent extraction procedures. There is no fault to find with the theoretical discussion, but I question the necessity for its inclusion in a practical handbook when so much of it is common knowledge or readily available already. For example, the contamination of samples during grinding is a danger common to all trace analysis, and has no special relevance to solvent extraction/flame spectroscopy.

The longest chapter is on applications, and to my mind suffers from a lack of critical appraisal of the work referenced and from the attitude expressed in the first two lines. They refer to an analyst "wishing to apply solvent extraction/flame spectroscopy to a particular sample", presumably for its own sake; of the 56 elements covered, reading the author's own comments suggests that nearly half would be better determined by a different technique. The lack of criticism has led to inconsistencies even within sections; under arsenic, the first reference is to "detection limits of 0.1 $\mu g\ ml^{-1}$ (or worse)", and 25 lines later to "an excellent detection limit of 0.07 $\mu g\ ml^{-1}$".

I would also have very much liked to see some recommendations based on Dr. Cresser's own wide experience of solvent extraction, rather than the mere blanket reporting of large numbers of systems to be found in the literature. Most of us use this type of monograph for guidance, and it is lacking.

Overall, I would not buy the book at this price; as an analyst I would prefer to use a text on solvent extraction procedures in general and to decide for myself whether a flame finish would be advantageous or not.

R. C. ROONEY

Volume 5 of the same series. In his preface Dr. Reid points out "It may encourage journal referees to press authors for methodological *rationale* rather than recipes", and the book itself lives up to this standard. In early chapters emphasis is placed on the importance of Quality Control and Sources of Error (Scales), and of the value of Internal Standardization (Curry and Whelpton). The chapter on Glass Capillary GC by Grob is profoundly workmanlike, and it is refreshing to meet such down-to-earth subheadings as 'Dirt in parts of the GC assembly'. Schill contributes a useful chapter on Ion-pair HPLC, and Kissinger's observations on Reverse Phase HPLC with Amperometric Detection reminded the reviewer of long forgotten electrochemistry. Scattered throughout the text are interesting case histories including one on the TCDD incident at Seveso. The book concludes with a useful Index of Compound Types which back references also to Volume 5. Apart from a very few typographical errors the only criticism which might be offered is that it would have been preferable to have the "Comments and Dialogue" appended to each chapter rather than to isolate these at the end of the book. This is essentially a "tips" book, and as such should be in any departmental library where this kind of analytical work is done. For its content the cost is not high.

W. B. YEOMAN

GLC and HPLC Determination of Therapeutic Agents, Part 1: K. TSUJI and W. MOROZOWICH (eds.), Dekker, New York, 1978. Pp. xiv + 415. S.Fr. 98.00.

This is the first part of a three-volume work devoted to analysis by gas and liquid chromatography. The three parts together will constitute Volume 9 of the series describing various aspects of chromatography. The text is arranged in thirteen chapters, written by no less than twenty-two authors, each chapter being concerned with some particular facet of the application of the twin techniques to the assay of therapeutic substances. Much of this material has been reviewed before, both in the literature and in numerous books. This applies particularly to the chapters dealing with the theory of gas chromatography, the properties of stationary phases and the coupling of mass spectrometers with gas chromatographs. Less familiar will be those sections outlining the use of derivatives in HPLC and the application of the mass spectrometer as a detector in HPLC. In the latter case the technology in this particular form of instrumentation is advancing at a rapid rate and the inclusion of the most recent developments is welcome. Other topics reviewed in detail in succeeding chapters are the scaling-up of chromatographic methods for preparative purposes, the automation of chromatographic systems and the use of computers for processing chromatographic data. This will be a useful book for the practising analytical chemist, bringing together as it does information on the two complementary chromatographic techniques and providing a valuable survey of sample pre-treatment methods.

J. R. MAJER

background of a method. To give but three examples, the rearrangement of penicillin sulfoxide to cephalosporins is discussed without mention of the seminal work of Morin and the Lilly Laboratories; the alkylation of carbanions to thiolsulfonates is discussed with no references to Smiles; the contribution of Tsuji in the use of palladium complexes to form carbon–carbon bonds is mentioned, but there is no suggestion of its pioneering nature. This is not so much a criticism as a reminder to the users of the book.

The book is not especially concerned with mechanism and its usefulness is, therefore, not really affected by the (very few) questionable statements one inevitably encounters, such as comments on the addition of benzoylsulfene (p. 419), on the reason for the formation of allylic alcohols from selenoxides (compare p. 494 with p. 501), on what is, perhaps unfortunately, termed 1,3-additions to carbonyl compounds (p. 981), on the nature of Zn enolates (p. 992). *Misleading* statements are, as one would expect, extremely rare, one such concerning the suggested generality of the addition of Grignard reagents to imines.

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Part 22 Nucleic Acids, by G. M. Blackburn; Nucleosides, by R. T. Walker; Nucleotides and Related Organic Phosphates, by D. W. Hutchinson; Nucleic Acids: Structure and Function, by G. M. Blackburn. Reviewed with G. W. Daub. Besides providing the organic chemist with a good exposure to fundamentals of the field, new developments and some of the more sophisticated aspects are treated to promote understanding at a higher level. The coverage includes work up through 1977.

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Talanta. Vol. 26. p. v
Pergamon Press Ltd., 1979. Printed in Great Britain

ERRATA

In the paper by D. Klockow, G. F. Graf and J. Auffarth, *Talanta*, 1979, **26**, 733, the term "ppM" (parts per milliard) should be replaced wherever it occurs, by the term "ppm" (parts per million) as originally written by the authors, and the definition of ppM given in the "Reagents" section on p. 734 should be deleted.

The title of the paper by R. N. Reddie and D. E. Peters, *Talanta*, 1979, **26**, 389, should read:

AN EVALUATION OF METHODS OF ANALYSIS FOR ALKYLAMINO-OXOMETHANE SULPHONATES

Talanta Vol. 26, p. v
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ERRATUM

In the paper by J. E. Kessler, S. M. Vincent and J. E. Riley, Jr., *Talanta*, 1979, **26**, 21, the following corrections are necessary.
Page 22, Fig. 2, item (4) is a 0.045 μm filter (not 0.22 μm), item (6) is a 10 μm disc.
Page 23, left-hand column, first line, delete "wall".
The missing information in reference 12 is 1978, **50**, 541, and in reference 14 is 1978, **50**, 164.

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Part 25 Lipid Chemistry and Biochemistry: Fatty Acids, by F. D. Gunstone; Lipids, by F. D. Gunstone; Membranes and Lipoproteins, by P. F. Knowles. Reviewed with H. M. McConnell. This is a first-class treatment of the subject. Even from the point of view of the biochemist or biophysicist its weaknesses are principally matters of omission. It is perhaps worth noting that these latter scientists would regard cholesterol (as well as natural derivatives of fatty acids) as a lipid. One also might question the implication that the majority of proteins occurring in membranes are enzymes. Be that as it may, this is a splendid exposition of the subject for a chemical audience.

Part 26 Carbohydrate Chemistry: Monosaccharide Chemistry, by L. Hough and A. C. Richardson; Oligosaccharide Chemistry, by L. Hough and A. C. Richardson; Polysaccharides, by J. F. Kennedy and C. A. White; Polysaccharides: Conformational Properties in Solution, by D. A. Rees. Reviewed with G. A. Crosby. In addition to a clear and concise treatment of monosaccharide chemistry, an interesting section on sugars containing heteroatoms is included, i.e. amino- and halosugars. A timely addition would have been some illustration of the use of sugars as chiral synthons and templates for asymmetric synthesis of natural products. The four-page section on oligosaccharide chemistry is probably too brief as it barely touches on the subject. The polysaccharide section is especially good and up-to-date (48% of the references $\geq$ 1970). More attention could have been given to reactions of polysaccharides. The section on conformation seems to be very good and up-to-date (95% of the references $\geq$ 1970).

Part 27 Synthesis of Organic Macromolecules and their Uses in Organic Chemistry, by P. Hodge. Reviewed with G. A. Crosby. This section is well-written, easy to comprehend, accurate and interesting. However, the coverage is too brief (30 pages) and some important topics are almost ignored. For example, the treatment of the synthesis and properties of macromolecules covers only 19 pages as compared with 40 in Roberts and Caserio's *Basic Principles of Organic Chemistry* (2nd ed.). In the section on applications, the treatment of cross-linked polymers is excellent, but there are some other important subjects which could have been covered, including reactions of soluble polymers and selected industrial applications.

Part 28 Bio-Organic Chemistry: Biosynthesis, by R. Thomas; Photosynthesis, Nitrogen Fixation and Intermediary Metabolism, by E. Haslam. Part 29 Biosynthetic Pathways from Acetate: Polyketide Biosynthesis, by J. D. Bu'Lock; Terpenoid Biosynthesis, by J. R. Hanson; Carotenoid Biosynthesis and Vitamin A, by G. Britton. Part 30 Biosynthesis—A General Survey: Alkaloid Biosynthesis, by R. B. Herbert; Porphyrin, Chlorophyll, and Corrin Biosynthesis, by M. Akhtar and P. M. Jordan; Shikimic Acid Metabolites, by E. Haslam. Reviewed with R. J. Parry. Aside from a slight organizational problem, i.e. all of Part 29 seemingly belongs under the heading of Part 30, these chapters are extremely well-written. The material is quite up-to-date through 1975, and the important aspects of the field have been covered in a scholarly manner. In seeking perfection one can find only minor areas for improvement, i.e. Chart 2 on page 919 and Chart 4 on page 925, particularly the former, are difficult to interpret; in Scheme 7, p. 1053, it is incorrectly implied that the mechanism of reduction of the pyridine ring of nicotinic acid has been established; the representation of the adduct of thiamine pyrophosphate and α-ketoglutaric acid (in Schemes 16, 33 and 34, pp. 1184, 1200 and 1201) as a naked carbonion (having acidic hydrogens) is not very satisfactory.

In conclusion, Haslam and his collaborating coauthors are to be congratulated for producing such a magnificent segment of the Barton–Ollis magnum opus which indeed represents a major contribution to scholars of organic chemistry.

To be reviewed by J. E. Baldwin, FRS, *Oxford*:
Volume 6 (Author, Formula, Subject, Reagent, Reaction Indexes; edited by C. J. Drayton, *Oxford*).
This review will be published in a subsequent issue.

Comprehensive Organic Chemistry is published in six volumes (approximately 8000 pages) by Pergamon Press, Oxford and New York. Price US $1250 (£625).

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NOTICES

FECHEM CONFERENCE
COMPUTER-BASED ANALYTICAL CHEMISTRY

24–28 September 1979, Portorož, Yugoslavia

The main topics will be:

fundamentals of computerization of analytical laboratories,
principles and problems of computer-based instruments and networks,
analytical information systems (storage, retrieval and computer-based interpretation of instrumental data),
special topics in computer-based analytical procedures.

Information from Dr. Jure Zupan, Boris Kidrič Institute of Chemistry, 61001 Ljubljana, P.O. Box 380, Yugoslavia.

J. HEYROVSKÝ MEMORIAL CONGRESS ON POLAROGRAPHY

25–29 August 1980, Prague, Czechoslovakia

The Congress is to take place on the occasion of the 90th anniversary of the birth of Professor Heyrovský and the 30th anniversary of the foundation of the Heyrovský Institute of Physical Chemistry and Electrochemistry of the Czechoslovak Academy of Sciences. The aim of the Congress is to survey the present state of polarography and related methods in the fields of basic research, contemporary instrumental techniques and analytical chemistry, and applications in industry, biology, medicine and environmental science. The Congress will be organized in two parallel sections. The main topics will be outlined in five plenary and twelve section lectures. Related groups of problems will be discussed in five microsymposia and four panel discussions. Contributed papers will be given in poster form and accepted in almost unlimited number. Final applications for participation must be sent before 30 November 1979. Information from the Secretariat of the J. Heyrovský Memorial Congress on Polarography, Vlašská 9, 118 40 Prague 1, Czechoslovakia.

HUNGARIAN CHEMICAL SOCIETY
4th SYMPOSIUM ON ION-EXCHANGE

27–30 May 1980, Lake Balaton, Hungary

The topics will be:

ion-exchange materials,
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